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VOLUME III AND IV

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INTERIM FINAL

RCRA FACILITY INVESTIGATION (RFI) GUIDANCE

VOLUME III OF IV

AIR AND SURFACE WATER RELEASES

EPA 530/SW-89-031

MAY 1989

WASTE MANAGEMENT DIVISION
OFFICE OF SOLID WASTE
U.S. ENVIRONMENTAL PROTECTION AGENCY

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SPRINGFIELD, VA 22161

ABSTRACT

On November 8, 1984, Congress enacted the Hazardous and Solid Waste Amendments (HSWA) to RCRA. Among the most significant provisions of HSWA are §3004(u), which requires corrective action for releases of hazardous waste or constituents from solid waste management units at hazardous waste treatment, storage and disposal facilities seeking final RCRA permits; and §3004(v), which compels corrective action for releases that have migrated beyond the facility property boundary. EPA will be promulgating rules to implement the corrective action provisions of HSWA, including requirements for release investigations and corrective measures.

This document, which is presented in four volumes, provides guidance to regulatory agency personnel on overseeing owners or operators of hazardous waste management facilities in the conduct of the second phase of the RCRA Corrective Action Program, the RCRA Facility Investigation (RFI). Guidance is provided for the development and performance of an investigation by the facility owner or operator based on determinations made by the regulatory agency as expressed in the schedule of a permit or in an enforcement order issued under §3008(h), §7003, and/or §3013. The purpose of the RFI is to obtain information to fully characterize the nature, extent and rate of migration of releases of hazardous waste or constituents and to interpret this information to determine whether interim corrective measures and/or a Corrective Measures Study may be necessary.

DISCLAIMER

This document is intended to assist Regional and State personnel in exercising the discretion conferred by regulation in developing requirements for the conduct of RCRA Facility Investigations (RFIs) pursuant to 40 CFR 264. Conformance with this guidance is expected to result in the development of RFIs that meet the regulatory standard of adequately detecting and characterizing the nature and extent of releases. However, EPA will not necessarily limit acceptable RFIs to those that comport with the guidance set forth herein. This document is not a regulation (i.e., it does not establish a standard of conduct which has the force of law) and should not be used as such. Regional and State personnel must exercise their discretion in using this guidance document as well as other relevant information in determining whether an RFI meets the regulatory standard.

Mention of company or product names in this document should not be considered as an endorsement by the U.S. Environmental Protection Agency.

RCRA FACILITY INVESTIATION (RFI) GUIDANCE

VOLUME III

AIR AND SURFACE WATER RELEASES

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LIST OF ACRONYMS

AA	-	Atomic Absorption
AI	-	Soil Adsorption Isotherm Test
ASCS	-	Agricultural Stabilization and Conservation Service
ASTM	-	American Society for Testing and Materials
BCF	-	Bioconcentration Factor
BOD	-	Biological Oxygen Demand
CAG	-	EPA Carcinogen Assessment Group
CPF	-	Carcinogen Potency Factor
CBI	-	Confidential Business Information
CEC	-	Cation Exchange Capacity
CERCLA	-	Comprehensive Environmental Response, Compensation, and Lability Act
CFR	-	Code of Federal Regulations
CIR	-	Color Infrared
CM	-	Corrective Measures
CMI	-	Corrective Measures Implementation
CMS	-	Corrective Measures Study
COD	-	Chemical Oxygen Demand
COLIWASA	-	Composite Liquid Waste Sampler
DNPH	-	Dinitrophenyl Hydrazine
DO	-	Dissolved Oxygen
DOT	-	Department of Transportation
ECD	-	Electron Capture Detector
EM	-	Electromagnetic
EP	-	Extraction Procedure
EPA	-	Environmental Protection Agency
FEMA	-	Federal Emergency Management Agency
FID	-	Flame Ionization Detector
Foc	-	Fraction organic carbon in soil
FWS	-	U.S. Fish and Wildlife Service
GC	-	Gas Chromatography
GC/MS	-	Gas Chromatography/Mass Spectroscopy
GPR	-	Ground Penetrating Radar
HEA	-	Health and Environmental Assessment
HEEP	-	Health and Environmental Effects Profile
HPLC	-	High Pressure Liquid Chromatography
HSWA	-	Hazardous and Solid Waste Amendments (to RCRA)
HWM	-	Hazardous Waste Management
ICP	-	Inductively Coupled (Argon) Plasma
ID	-	Infrared Detector
Kd	-	Soil/Water Partition Coefficient
Koc	-	Organic Carbon Absorption Coefficient
Kow	-	Octanol/Water Partition Coefficient
LEL	-	Lower Explosive Limit
MCL	-	Maximum Contaminant Level
MM5	-	Modified Method 5
MS/MS	-	Mass Spectroscopy/Mass Spectroscopy
NFIP	-	National Flood Insurance Program
NIOSH	-	National Institute for Occupational Safety and Health
NPDES	-	National Pollutant Discharge Elimination System
OSHA	-	Occupational Safety and Health Administration

LIST OF ACRONYMS (Continued)

OVA	-	Organic Vapor Analyzer
PID	-	Photo Ionization Detector
pKa	-	Acid Dissociation Constant
ppb	-	parts per billion
ppm	-	parts per million
PUF	-	Polyurethane Foam
PVC	-	Polyvinyl Chloride
QA/QC	-	Quality Assurance/Quality Control
RCRA	-	Resource Conservation and Recovery Act
RFA	-	RCRA Facility Assessment
RfD	-	Reference Dose
RFI	-	RCRA Facility Investigation
RMCL	-	Recommended Maximum Contaminant Level
RSD	-	Risk Specific Dose
SASS	-	Source Assessment Sampling System
SCBA	-	Self Contained Breathing Apparatus
SCS	-	Soil Conservation Service
SOP	-	Standard Operating Procedure
SWMU	-	Solid Waste Management Unit
TCLP	-	Toxicity Characteristic Leaching Procedure
TEGD	-	Technical Enforcement Guidance Document (EPA, 1986)
TOC	-	Total Organic Carbon
TOT	-	Time of travel
TOX	-	Total Organic Halogen
USGS	-	United States Geologic Survey
USLE	-	Universal Soil Loss Equation
UV	-	Ultraviolet
VOST	-	Volatile Organic Sampling Train
VSP	-	Verticle Seismic Profiling
WQC	-	Water Quality Criteria

SECTION 12

AIR

12.1 Overview

The objective of an investigation of a release to air is to characterize the nature, extent, and rate of migration of the release of hazardous waste or constituents to that medium. This is done by characterizing long-term air concentrations (commensurate with the long-term exposures which are the basis for the health and environmental criteria presented in Section 8) associated with unit releases of hazardous wastes or constituents to air. This section provides:

- An example strategy for characterizing releases to air, which includes characterization of the source and the environmental setting of the release, and conducting a monitoring and/or modeling program which will characterize the release itself;
- Formats for data organization and presentation;
- Modeling and field methods which may be used in the investigation; and
- A checklist of information that may be needed for release characterization.

The exact type and amount of information required for sufficient release characterization will be site-specific and should be determined through interactions between the regulatory agency and the facility owner or operator during the RFI process. This guidance does not define the specific data needed in all instances; it identifies possible information necessary to perform release characterizations and methods for obtaining this information. The RFI Checklist, presented at the end of this section, provides a tool for planning and tracking information for release characterization. This list is not a list of requirements for all releases to air. Some release investigations will involve the collection of only a subset of the items listed, while other releases may involve the collection of additional data.

Case studies 25 and 26 in Volume IV (Case Study Examples) illustrate several of the air investigation concepts discussed in this section.

12.2 Approach for Characterizing Releases to Air

12.2.1 General Approach

The intent of the air release investigation is to determine actual or potential effects at the facility property boundary. This differs from the other media discussed in this Guidance. During the health and environmental assessment process for the air medium (see Section 8), the decision as to whether interim corrective measures or a Corrective Measures Study will be necessary is based on actual or potential effects at the facility property boundary.

Characterization of releases from waste management units to air may be approached in a tiered or phased fashion as described in Section 3. The key elements to this approach are shown in Table 12-1. Tasks for implementing the release characterization strategy for releases to air are summarized in Table 12-2. An overview of the release characterization strategy for air is illustrated in Figures 12-1 through 12-5.

Two major elements can be derived from this strategy:

- Collection and review of data to be used for characterization of the source of the air release and the environmental setting for this source. Source characterization will include obtaining information on the unit operating conditions and configuration, and may entail a sampling and analytical effort to characterize the waste material in the unit or the incoming waste streams. This effort will lead to development of a conceptual model of the release that provides a working hypothesis of the release mechanism, transport pathway/mechanism, and exposure route (if any), which can be used to guide the investigation.

- Development and implementation of modeling and/or monitoring procedures to be used for characterization of the release (e.g., from a

TABLE 12-1

EXAMPLE STRATEGY FOR CHARACTERIZING RELEASES TO AIR*

INITIAL PHASE

1. Collect and review existing information on:

   - Waste
   - Unit
   - Environmental setting (e.g., climate, topography)
   - Contaminant releases, including inter-media transport
   - Receptors at and beyond the facility property boundary

2. Identify additional information necessary to fully characterize release:

   - Waste
   - Unit
   - Environmental setting (e.g., climate, topography)
   - Contaminant releases, including inter-media transport
   - Receptors at and beyond the facility property boundary

3. Conduct screening assessments:

   - Formulate conceptual model of release
   - Determine monitoring/modeling program objectives
   - Obtain source characterization data needed for modeling input
   - Select release constituent surrogates
   - Calculate emission estimates based on emission rate screening modeling results
   - Calculate concentration estimates based on dispersion screening modeling results
   - Compare results to health based criteria
   - Conduct screening monitoring at source (as warranted)
   - Perform sensitivity analysis of modeling input/output
   - Obtain additional waste/unit data as needed for refined modeling
   - Consider conduct of more refined emission/dispersion modeling

4. Collect, evaluate and report results:

   - Account for unit/waste temporal and spatial variability and modeling input/output uncertainties
   - Determine completeness and adequacy of screening assessment results
   - Evaluate potential for inter-media contaminant transfer
   - Summarize and present results in appropriate format
   - Determine if monitoring program objectives were met
   - Compare screening results to health and environmental criteria and identify and respond to emergency situations and identify priority situations that may warrant interim corrective measures - Notify regulatory agency
   - Determine whether the conduct of subsequent release charaterization phases are necessary to obtain more refined concentration estimates

TABLE 12-1 (continued)

EXAMPLE STRATEGY FOR CHARACTERIZING RELEASES TO AIR*

SUBSEQUENT PHASES (if necessary)

1. Conduct emission monitoring and dispersion modeling if necessary:

   - Conduct onsite meteorological monitoring if representative data are not available for dispersion modeling input
   - Conduct emission rate monitoring
   - Conduct dispersion modeling using emission rate monitoring data as input
   - Evaluate results and determine need for confirmatory air monitoring

2. Conduct confirmatory air monitoring if necessary:

   - Develop monitoring procedures
   - Conduct initial monitoring
   - Conduct additional monitoring if additional information is necessary to characterize the release

3. Collect, evaluate and report results:

   - Account for source and meteorological data variability during modeling and monitoring program
   - Evaluate long-term representativeness of air monitoring data
   - Apply dispersion models as appropriate to aid in data evaluation and to provide concentration estimates at the facility property boundary
   - Compare monitoring results to health and environmental criteria and identify and respond to emergency situations and identify priority situations that may warrant interim corrective measures - Notify regulatory agency
   - Determine completeness and adequacy of collected data
   - Summarize and present data in appropriate format
   - Determine if modeling and monitoring locations, constituents, and frequency were adequate to characterize release (nature, extent, and rate)
   - Determine if monitoring/modeling program objectives were met
   - Identify additional information needs, if necessary
   - Determine need to expand modeling and monitoring program
   - Evaluate potential role of inter-media transport

* The potential for inter-media transport of contamination should be evaluated continually throughout the investigation.

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TABLE 12-2
RELEASE CHARACTERIZATION TASKS FOR AIR

Investigatory Tasks	Investigatory Techniques	Data Presentation Formats/Outputs
1. Waste/Unit Characterization		
- Identification of waste constituents and properties	- See Section 3, 7 and Volume I, Appendix B List 2; Section 12.3, Section 12.4, Appendix F	- Listing of potential release constituents
- Prioritization of air emission constituents	- Waste sampling and characterization	- Listing of target air emission constituents for monitoring
- Identification of unit characteristics which may promote an air release	- See Section 7, Section 12.3, Section 12.4, Appendix F	- Description of the unit
2. Environmental Setting Characterization		
- Definition of climate	- Climate summaries for regional National Weather Service stations (may require onsite meteorological monitoring survey)	- Wind roses and statistical tabulations for parameters of interest
- Definition of site-specific meteorological conditions	- Onsite meteorological monitoring concurrent with air monitoring	- Wind roses and tabulations for parameters of interest
- Definition of soil conditions to characterize emission potential for particulate emissions and for certain units (e.g., landfills and land treatment) for gaseous emissions	- See Section 9	- Soil physical properties (e.g., porosity, organic matter content)
- Definition of site-specific terrain	- See Section 7, 9 and Appendix A (Volume 1) of RFI and recent aerial photographs and U.S. Geolgoical Survey maps	- Topographic map of site area
- Identification of potential air-pathway receptors	- Census data, area surveys, recent aerial photographs and U.S. Geological Survey topographic maps	- Map with identification of nearby populations and buildings
3. Release Characterization		
- Emission rate modeling	- Air emission models as discussed in Section 12.4	- Unit-specific and constituent-specific emission rates
- Dispersion modeling	- Atmospheric dispersion models as discussed in Section 12.5	- Air concentration estimates at facility property boundary (tabular summaries or graphical presentations which may include release concentration isopleths)
- Emission rate monitoring	- Direct emission source tests for point sources, isolation flux chamber for area sources or onsite air monitoring (Section 12.8)	- Listing of emission rate monitoring results
- Air monitoring	- Upwind/downwind air monitoring for "release mapping"	- Air concentration estimates at facility property boundary (tabular summaries or graphical presentations which may include release concentration isopleths)

FIGURE 12-1
RELEASE CHARACTERIZATION STRATEGY FOR AIR-OVERVIEW

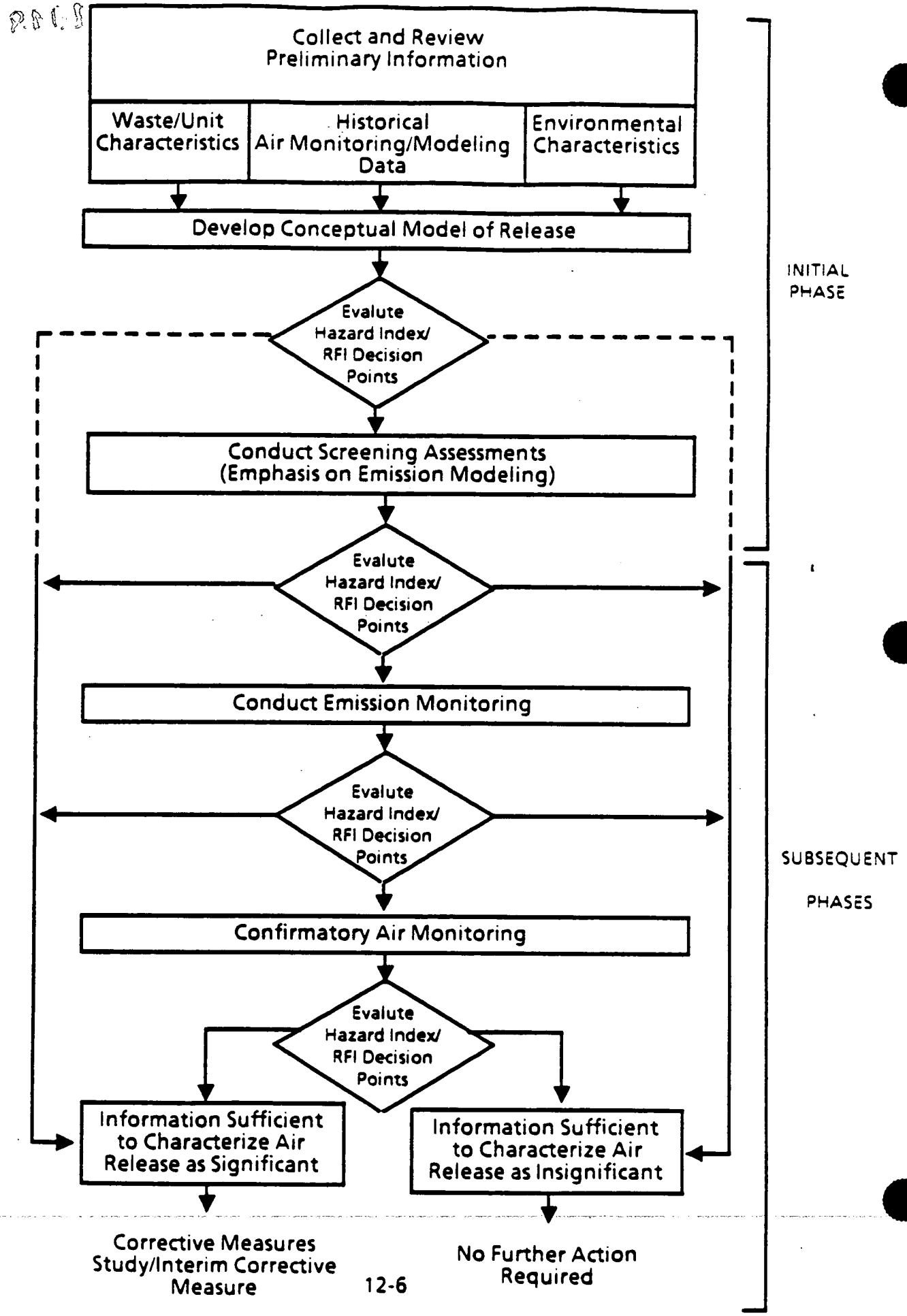

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FIGURE 12-2
CONDUCT SCREENING ASSESSMENTS - OVERVIEW

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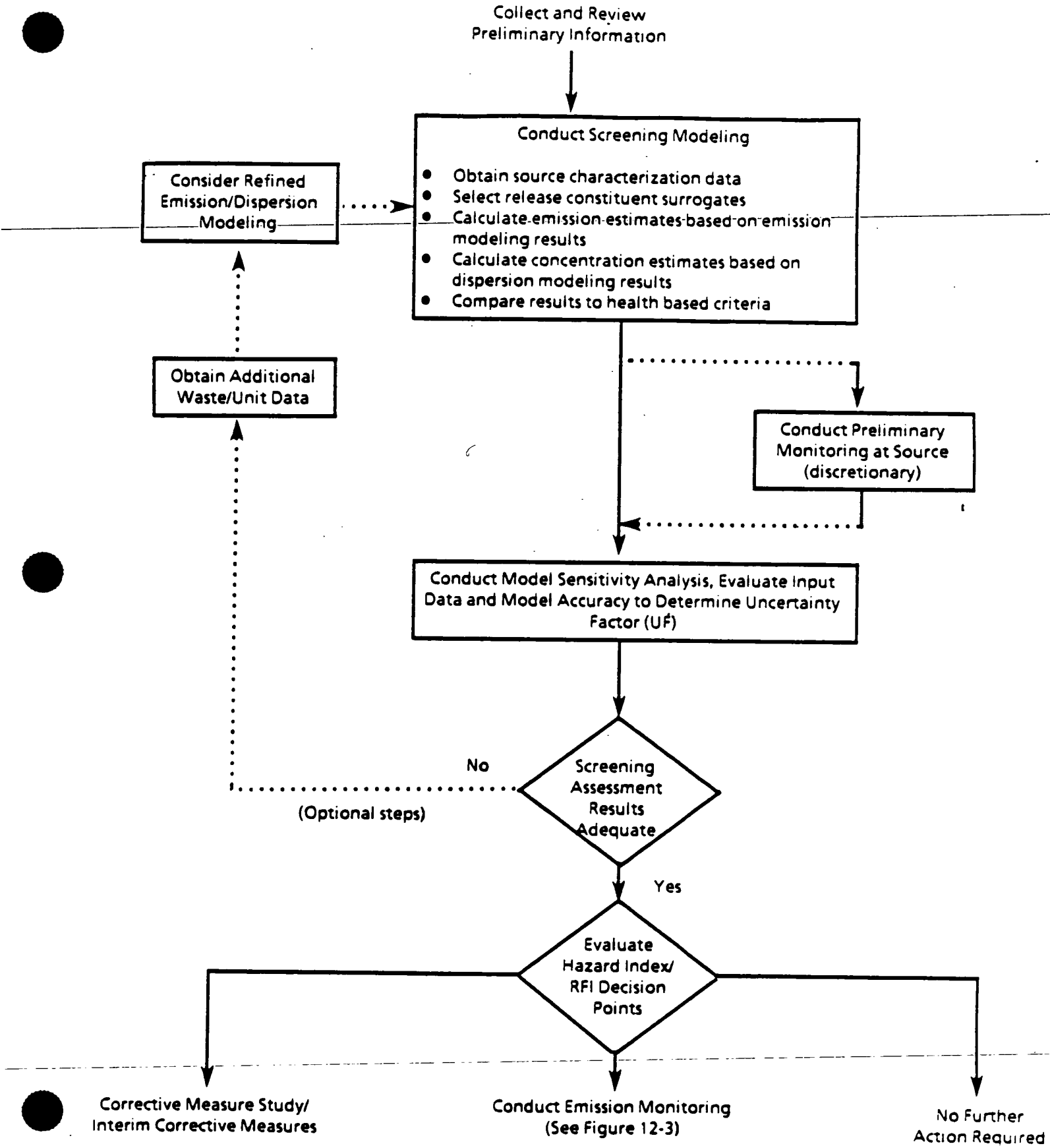

FIGURE 12-3
CONDUCT EMISSION MONITORING - OVERVIEW

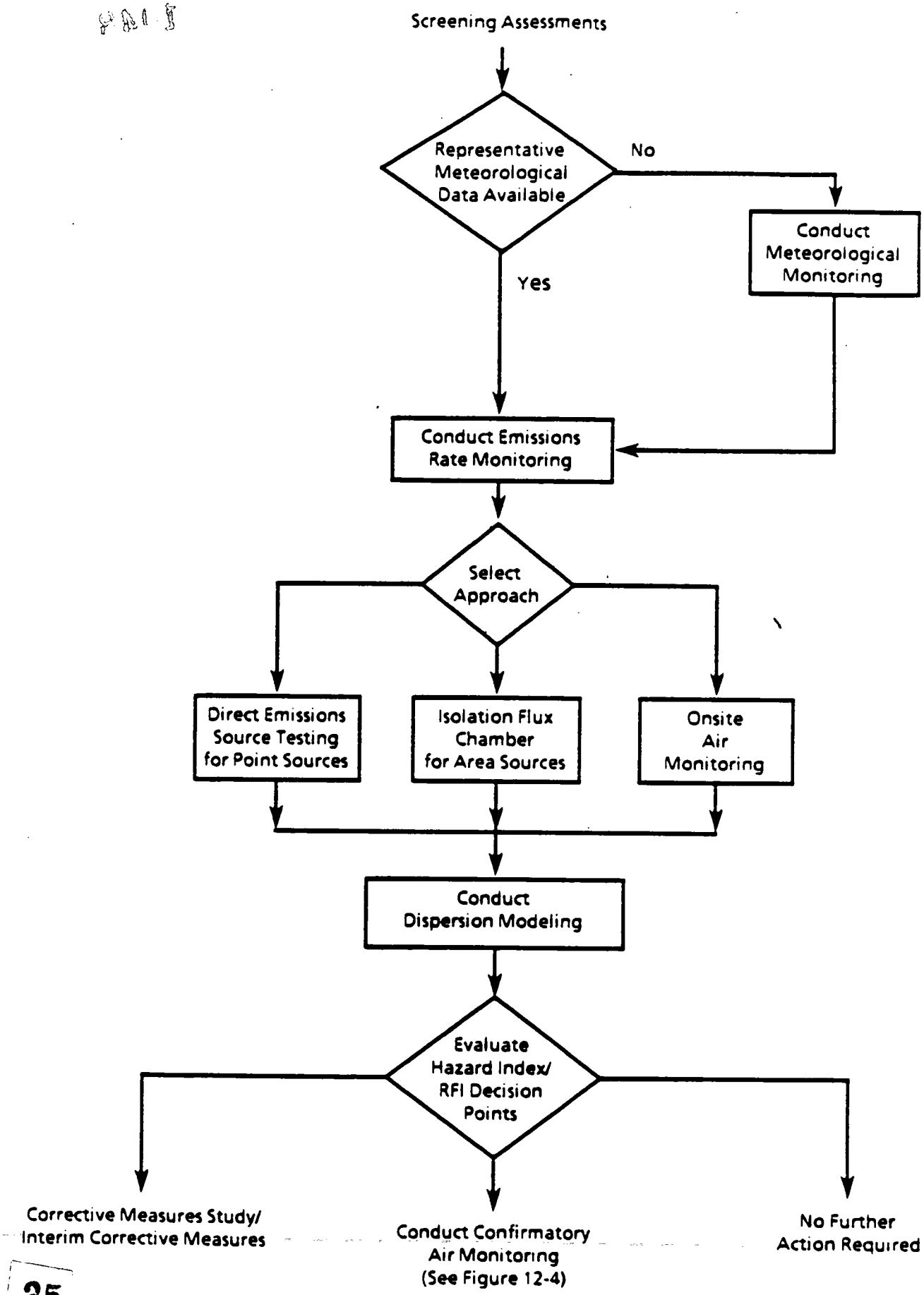

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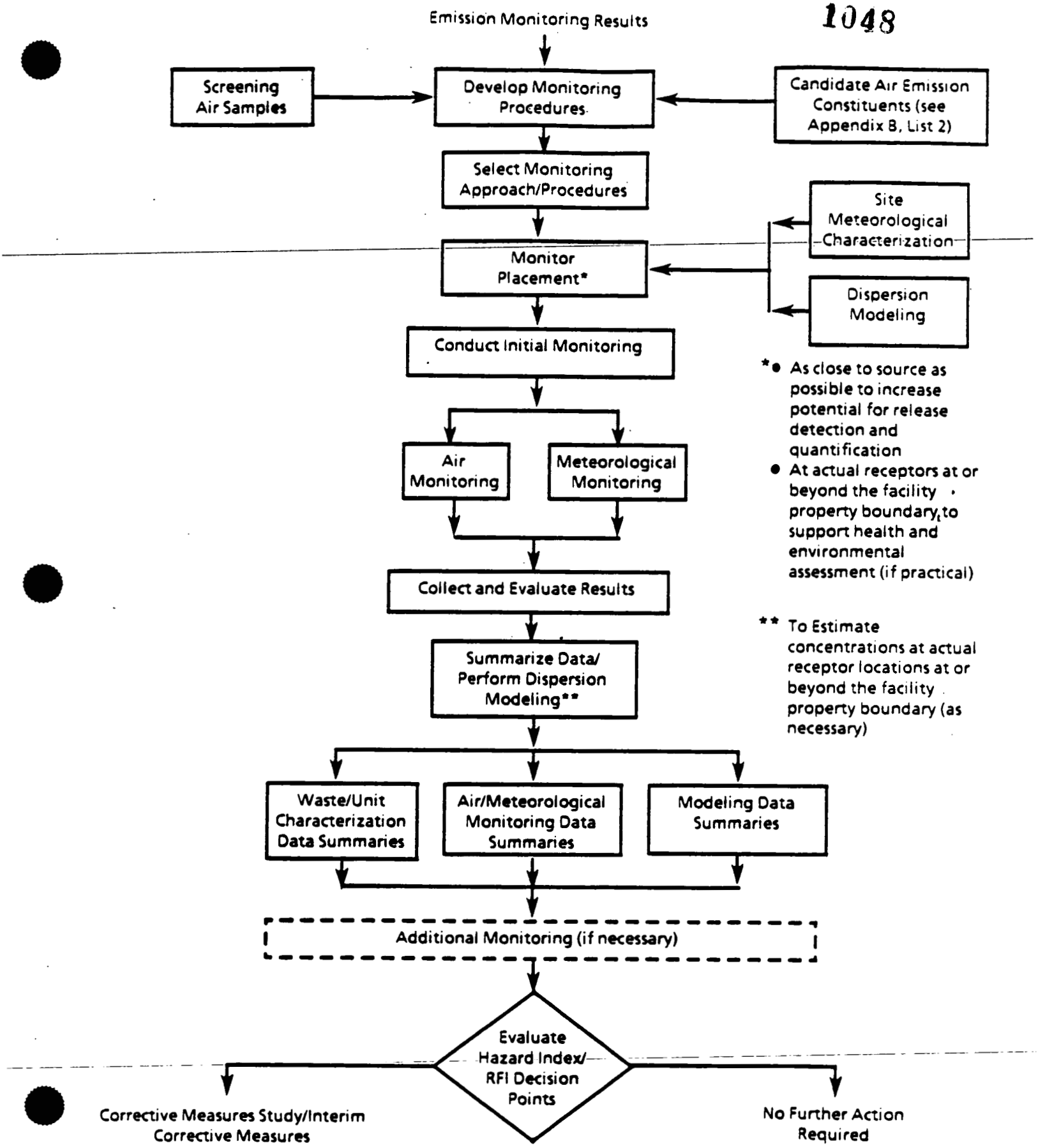
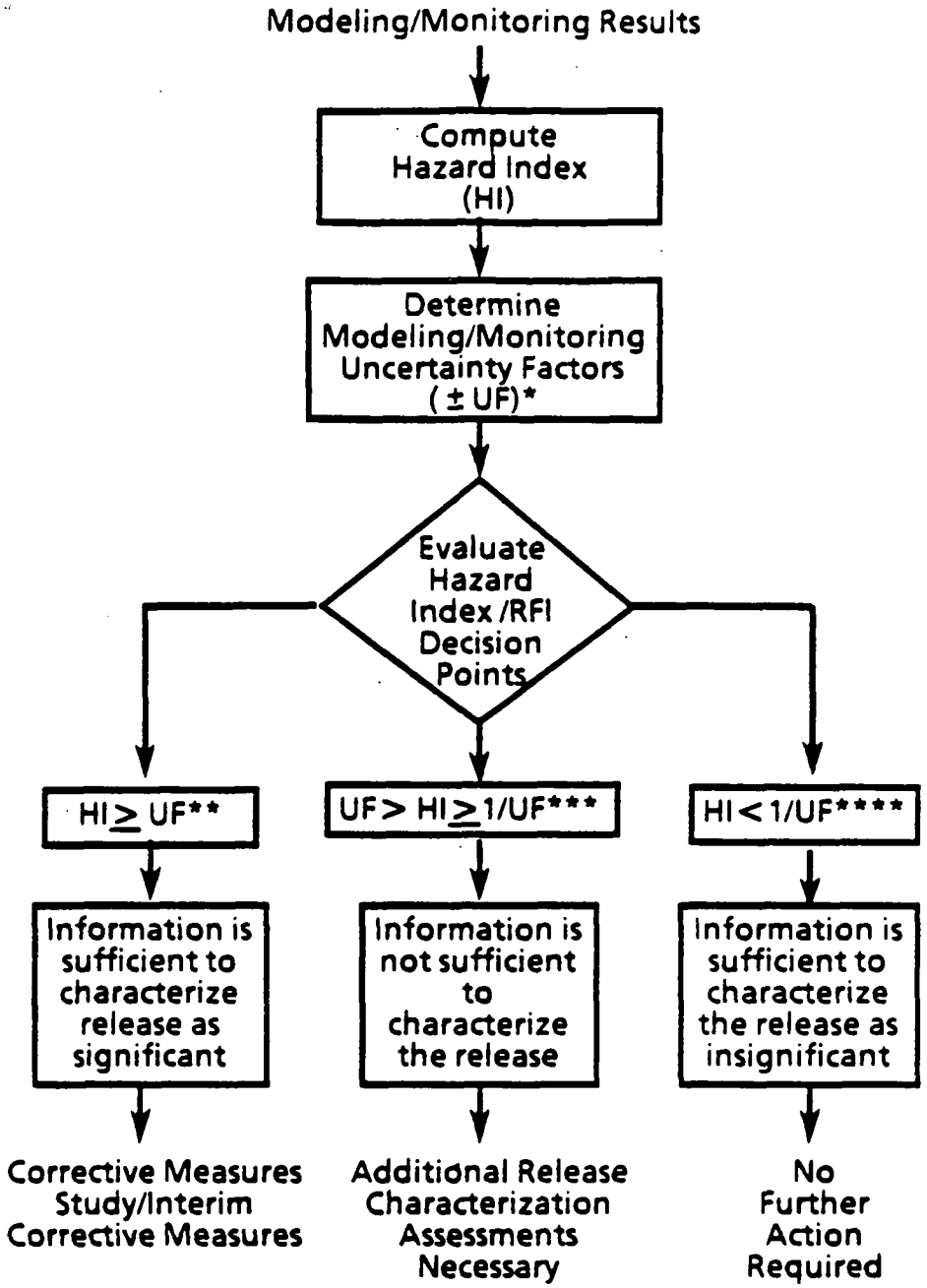
FIGURE 12-4
CONDUCT CONFIRMATORY AIR MONITORING



* • As close to source as possible to increase potential for release detection and quantification
• At actual receptors at or beyond the facility property boundary, to support health and environmental assessment (if practical)

** To Estimate concentrations at actual receptor locations at or beyond the facility property boundary (as necessary)

FIGURE 12-5
EVALUATION OF MODELING/MONITORING RESULTS



* Uncertainty Factor assumed to be ≥1.0

** HI ≥ 1 Generally used for evaulation of confirmatory air monitoring results.

*** This alternative is generally not used to evaluate confirmatory air monitoring results. However, additional air monitoring may be warranted if monitoring objectives were not acheived. Confirmatory air monitoring will generally be conducted during worst-case long-term emission/dispersion conditions. Therefore, this facilitates the use of more rigorous evaluation criteria for this final air release characterization step prior to RFI decisionmaking.

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**** HI < 1 Criterion generally used for evaluation of confirmatory air monitoring results.

unit or contaminated soil). Utilizing a phased approach, the air release is characterized in terms of the types and amounts of hazardous constituents being emitted, leading to a determination of actual or potential exposure at the facility property boundary. This may involve emission modeling (to estimate unit-specific emission rates), air monitoring (to determine concentrations at the facility property boundary), emission monitoring (monitoring at the source to determine emission rates), and dispersion modeling (to estimate concentrations at the facility property boundary). A phased approach utilizing both modeling and monitoring may not always be necessary to achieve adequate release charterization.

As indicated in Section 1 of this Guidance (See Volume I), standards for the control and monitoring of air emissions at hazardous waste treatment, storage and disposal (TSD) facilities are being developed by the Agency pursuant to HSWA Section 3004(n). These standards will address specific methodologies and regulatory requirements for the identification and control of air releases at TSD facilities. The Guidance provided herein is intended to provide interim methodologies and procedures for the identification and delineation of significant air releases. In particular, the Guidance addresses those releases which may pose an existing and significant hazard to human health and the environment, and thus, should be addressed without delay, i.e., prior to the issuance of the Section 3004(n) regulations.

The RFI release characterization strategy for air includes several decision points during the characterization process to evaluate the adequacy of available information and to determine an appropriate course of action from the following alternatives (as illustrated in Figures 12-1 through 12-5).

- Information is sufficient to characterize the air release as significant and a Corrective Measures Study/Interim Corrective Measures is warranted.

- Information is sufficient to characterize the air release as insignificant, therefore, no further air assessments are required.

- Information is not sufficient to characterize the air release, therefore further release characterization is warranted.

Criteria for decisionmaking involves consideration of the uncertainty associated with release characterization results (modeling/monitoring), which is facilitated by use of a Hazard Index as illustrated in Figure 12-5. The Hazard Index is defined as the ratio of exposure concentration levels or estimates, to specific health criteria for an individual constituent or a mixture of constituents with similar potential health impacts. Further guidance on the computation and application of the Hazard Index is provided in Section 8.

The uncertainty associated with concentration estimates based on air pathway modeling and monitoring results is factored into the decision making effort through use of uncertainty analyses. A primary component of the uncertainty analysis is the accuracy of the modeling and/or monitoring approach utilized for the release characterization. Model-specific and monitoring method-specific accuracies should be used as available for the uncertainty analysis. The quality of the input data to models is another important component of the uncertainty analysis that should be accounted for. Generally, conduct of a model sensitivity analysis (i.e., varying the values of input parameters based on their uncertainty range to evaluate the effect on model output), will provide a quantitative basis to characterize input data quality. This step is particularly important for some unit-specific models. For example, the spatial variability of wastes at a landfill and the uncertainty of other input parameters (e.g., soil porosity) can significantly affect the overall uncertainty associated with emission modeling results.

As concentration measurements or estimates at the facility property boundary become available, both within and at the conclusion of discrete investigation phases, they should be reported to the regulatory agency as directed. The regulatory agency will compare the concentrations with applicable health and environmental criteria to determine the need for (1) interim corrective measures; and/or (2) a Corrective Measures Study. In addition, the regulatory agency will evaluate the data with respect to adequacy and completeness to determine the need for any additional characterization efforts. The health and environmental criteria and a general discussion of how the regulatory agency will apply them are

provided in Section 8. A flow diagram illustrating RFI Decision Points is provided in Section 3 (See Figure 3-2).

Notwithstanding the above process, the owner or operator has a continuing responsibility to identify and respond to emergency situations and to define priority situations that may warrant interim corrective measures. For these situations, the owner or operator is advised to follow the RCRA Contingency Plan requirements under 40 CFR Part 264, Subpart D and Part 265, Subpart D.

The strategy for characterizing releases to air consists of an initial phase and, if necessary, subsequent phases, as illustrated in Table 12-1 and Figure 12-1. Additional phases may not be needed depending on the site-specific modeling/monitoring data available, and the nature and magnitude of the release. A summary discussion of the initial phase is presented in Section 12.2.1.1 and the subsequent phases in Section 12.2.1.2.

12.2.1.1 Initial Phase

The initial phase of the release characterization strategy for air involves the collection and review of preliminary information and the conduct of a screening assessment.

12.2.1.1.1 Collect and Review Preliminary Information

The first step is to collect, review and evaluate available waste, unit, environmental setting and release (monitoring and modeling) data. The air pathway data collection effort should be coordinated, as appropriate, with similar efforts for other media investigations.

Evaluation of these data may, at this point, clearly indicate that a Corrective Measures Study and/or interim corrective measures are necessary or that no further action is required. For example, the source may involve a large, active storage surface impoundment containing volatile constituents located adjacent to residential housing. Therefore, action instead of further studies may be appropriate. Another case may involve a unit in an isolated location, where an acceptable modeling/monitoring data base may be available which definitively

indicates that the air release can be considered insignificant and therefore further studies are not warranted. In most cases, however, further release characterization will be necessary.

A conceptual model (as discussed in Volume I - Summary Section and Section 3.2) of the release should then be developed based on available information. This model (not a computer or numerical simulation model) should provide a working hypothesis of the release mechanism, transport pathway/mechanism, and exposure route (if any). The model should be testable/verifiable and flexible enough to be modified as new data become available. For example, transport pathway and exposure modes for a contaminated surface area may involve air emissions due to volatilization, wind erosion and mechanical disturbances. These air emissions are expected to result in inhalation exposure for offsite receptors. In addition, the deposition of air emissions on soil, water bodies and crops, and infiltration and runoff from the onsite source, may contribute to overall exposures.

12.2.1.1.2 Conduct Screening Assessment

Following review of existing information and development of the conceptual model, a screening assessment should be conducted to characterize the air release (see Figure 12-2). The initial screening should be based on conservative (i.e., worst-case assumptions). A screening assessment based on more realistic assumptions should be conducted if initial air concentration predictions exceed health criteria.

The Draft Final Air Release Screening Assessment Methodology, presented in Appendix G, describes the screening assessment in detail. It consists of emission rate and dispersion models and involves the following steps:

- Obtain source characterization input data
- Select release (target) constituents which may be present in the waste and have health criteria for the air pathway (see Section 8.0)
- Calculate emission estimates
- Calculate concentration estimates at facility property boundary
- Compare results to health based criteria

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In order to assure adequate source characterization input data, it may be necessary to collect additional waste/unit data. This may involve field sampling of the waste to identify waste constituents and determine concentration levels. At this early RFI stage, it may be more effective and conclusive to sample the wastes (with relatively higher concentration levels) instead of the release. In general, if obtaining source-specific data is not practical, conservative source assumptions should be used.

Preliminary monitoring at the source may also be conducted to aid in the evaluation of the screening/modeling results. Preliminary monitoring may involve the use of screening or quantitative methods, and is discussed in Section 12.6. The preliminary monitoring period will generally be limited to a few days. Although preliminary monitoring results may identify release constituents that were not expected based on modeling, or vice versa, the limitations of modeling and monitoring should be considered when comparing these data and determining appropriate followup activities.

A sensitivity analysis should also be conducted to evaluate model input data quality. The results of the sensitivity analysis as well as consideration of model accuracy should be used to compute the UF for the screening assessment. The results of the screening assessment should then be compared to the health and environmental assessment criteria (as previously discussed) to determine appropriate followup actions. Collection of additional waste/unit data and/or considering the application of more refined emission/dispersion models are also possible options if initial results from the screening assessment are inconclusive.

12.2.1.2 Subsequent Phases

Subsequent phases of the release characterization strategy for air may be necessary if screening assessment results are not conclusive to characterize the air release, and should involve the conduct of emission monitoring and confirmatory air monitoring as indicated in Figure 12-1. These are discussed below.

PB.1.1

12.2.1.2.1 Conduct Emission Monitoring

Source monitoring should be used in conjunction with dispersion modeling to further characterize the release, as indicated in Figure 12.3. Direct emission sampling should be used for point sources such as vents and stacks. An isolation flux chamber may be used for area source emission measurements. Onsite air monitoring (particularly near the emission source) is an alternative approach for characterizing area source emissions if direct emission monitoring is not practical (e.g., considering equipment availability). Guidance for the conduct of these field programs is presented in Section 12.6 and 12.8.

The development of emission monitoring procedures should address selection of target air emission constituents. One acceptable approach is to monitor for all potential Appendix VIII air emission constituents (see Appendix B, List 3) applicable to the unit or release of concern. An alternative approach is to use unit and waste-specific information to identify constituents that are expected to be present, thus reducing the number of target constituents (see Section 3.6). The target constituents selected should be limited to those which may be present in the waste and have health criteria for the air pathway (see Section 8).

Representative meteorological data as well as emission monitoring results should be available as input data for dispersion modeling. Therefore, it may be necessary to conduct an onsite meteorological monitoring survey. The meteorological monitoring survey should be conducted, at a minimum, for a period sufficient to identify and define wind and stability patterns for the season associated with worst-case, long-term source emission/dispersion conditions. However, it may also be desirable to obtain sufficient data to characterize annual dispersion conditions at the site. The season associated with the highest long-term air concentration is determined by evaluating seasonal emission/dispersion modeling results based on available meteorological data (e.g., National Weather Service data). This modeling application accounts for the complex relationships between meteorological conditions and emissions potential and dispersion potential. For example, high average wind speeds may increase the long-term emission potential of organics at a surface impoundment, but worst case long-term dispersion conditions would be associated with low average wind speed conditions. Seasonal temperature conditions would also affect the emission potential.

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Therefore, it would be necessary to compare seasonal air concentration results to identify the season with worst case long term exposure conditions. This season would be the candidate period to collect several months of onsite meteorological data to support more refined modeling analyses (e.g., dispersion modeling using emission rate monitoring data as input). Guidance on selection of the emission monitoring period within this worst case season is presented in Section 12.6.4.2. Guidance on the conduct of a meteorological monitoring program is provided in Sections 12.6.3 and 12.8.1.

Dispersion models are used to estimate constituent concentrations based on source and meteorological monitoring input data. Guidance on the selection and application of dispersion models is presented in Section 12.5 and in Guidance on Air Quality Models (U.S. EPA, July 1986) and Procedures for Conducting Air Pathway Analyses for Superfund Applications (U.S. EPA, December 1988). The results of the dispersion modeling assessment should then be compared to the health and environmental assessment criteria (as previously discussed) to determine appropriate followup actions.

12.2.1.2.2 Confirmatory Air Monitoring

Confirmatory air monitoring (as outlined in Figure 12-4), may also be appropriate to provide additional release characterization information for RFI decisionmaking. Air monitoring data will provide a basis for release mapping and for evaluation and confirmation of modeling estimates. The conduct of an air monitoring program should include the following components:

- Develop monitoring procedures
- Conduct initial monitoring
- Collect and evaluate results
- Conduct additional air monitoring (if necessary)

The development of monitoring procedures should address selection of target air emission constituents. One acceptable approach is to monitor for all potential Appendix VIII air emission constituents (See Appendix B, List 3) applicable to the unit or release of concern. An alternative approach is to use unit and waste-specific information to identify constituents that are expected to be present, thus reducing

the number of target monitoring constituents (See Section 3.6). The target constituents selected should be limited to those which may be present in the waste and have health criteria for the air pathway (see Section 8.0).

The development of monitoring procedures should also include selection of appropriate field and analytical methods for conducting the air monitoring program. Candidate methods and criteria for monitoring program design (e.g., relevant to sampling schedule and monitor placement) should be limited to standard published protocols (such as those available from EPA, NIOSH, and ASTM). The selection of appropriate methods will be dependent on site and unit-specific conditions, and is discussed further in Section 12.8.

A limited screening-type sampling program may be appropriate for determining the design of the air monitoring program. The objective of this screening sampling will be to verify a suspected release, if appropriate, and to further assist in identifying and quantifying release constituents of concern. Screening sampling at each unit for a multiple-unit facility, for example, can be used to prioritize release sources. The emphasis during this screening will generally be on obtaining air samples near the source, or collecting a limited number of source emission samples. The availability of air monitoring data on units with a limited set of air emission constituents may preclude the need for screening sampling during the investigation.

An initial air monitoring program should be conducted, as necessary, to characterize the magnitude and distribution of air concentration levels for the target constituents selected. Initial monitoring should be conducted for a period sufficient to characterize air concentrations at the facility property boundary, as input to the health and environmental assessment (e.g., a 90-day period may be appropriate for a flat terrain site with minimal variability of dispersion and source conditions).

The basic approach for the initial air monitoring will consist of collection of ambient air samples for four target zones: the first zone located upwind of the source to define background concentration levels; the second zone located downwind at the unit boundary; the third zone located downwind at the facility property boundary for input into the health and environmental assessment; and a

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fourth zone offsite, as practical, to determine the need for interim corrective measures. Multiple monitoring stations will generally be required for each of the four target zones. It should be noted that offsite air monitoring may not always be practical due to various problems (e.g., vandalism, public tampering with equipment, public relations and legal access problems). Dispersion modeling can be used to estimate offsite concentrations if monitoring data are not available for the actual receptor locations of interest.

The location of air monitors within each zone should be based on site-specific diurnal and seasonal wind patterns appropriate for the monitoring period. An onsite meteorological monitoring survey (as previously discussed) may be necessary to characterize local wind patterns. The objective of the air monitoring network should be to provide adequate coverage for primary air flowpaths for each of the zones enumerated above.

The conduct of the initial air monitoring program generally includes the collection of meteorological data concurrent with air quality measurements. The meteorological data are needed during the air monitoring program to characterize emission potential and atmospheric dispersion conditions. This information is also used to evaluate source/receptor relationships and to interpret and extrapolate the air monitoring data.

Additional air monitoring may be warranted if initial monitoring program objectives are not met (e.g., data recovery goals were not adequate) or results are not adequate to characterize the release (e.g., additional monitoring stations are needed).

The air monitoring program data should be evaluated, and a dispersion model used, as needed, to estimate concentrations at the facility property boundary. These results should then be compared to the health and environmental assessment criteria (as previously discussed). Subsequent monitoring may also be conducted during or after the implementation of corrective measures to characterize changes in downwind release concentrations attributed to mitigation efforts.

12.3 Characterization of the Contaminant Source and the Environmental Setting

Release investigations can be conducted in an efficient, effective and representative manner if certain information is obtained prior to implementation of the effort. This information consists of both waste/unit characterization and characterization of the environmental setting. Review of information from existing sources can be used to identify data gaps and to initiate data collection activities to fill these data gaps. Waste/unit characterization and characterization of the environmental setting are discussed below:

> Waste and unit specific information: Data on the specific constituents present in the unit that are likely to be released to the air can be used to design sampling efforts and identify candidate constituents to be monitored. This information can be obtained from either a review of the existing information on the waste or from new sampling and analysis. The manner in which the wastes are treated, stored or disposed may have a bearing on the magnitude of air emissions from a unit. In many cases, this information may be obtained from facility records, contact with the manufacturer of any control devices, or, in some cases, from the facility's RCRA permit application.
>
> Environmental setting information: Environmental setting information, particularly climatological data, is essential in characterizing an air release. Climatological parameters such as wind speed and temperature will have a significant impact on the distribution of a release and in determining whether a particular constituent will be released. Climatological and meteorological information for the area in which the facility is located can be obtained either through an onsite monitoring effort or from the National Climatic Data Center (Asheville, NC). The climatological data should be evaluated considering site topography and other local influences that can affect the data representatives.

Information pertaining to the waste, unit, and environmental setting can be found in many readily available sources. General information concerning waste/unit characterization is discussed in Section 7. Air specific information is provided in the following discussions.

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12.3.1 Waste Characterization

Several waste characteristics contribute to the potential for a waste constituent to be released via the air pathway. These characteristics, in conjunction with the type of unit and its operation, will determine whether a release will be via volatilization of the constituent or as particulate entrainment. Major factors include the types and number of hazardous constituents present, the concentrations of these constituents in the waste(s), and the chemical and physical characteristics of the waste and its constituents. All of these factors should be considered in the context of the specific unit operation involved. It is important to recognize that the constituents of concern in a particulate release may involve constituents that are either sorbed onto the particulate, or constituents which actually comprise the particulate.

12.3.1.1 Presence of Constituents

The composition of the wastes managed in the unit of concern will influence the nature of a release to air. Previous studies may indicate that the constituents are present in the unit or that there is a potential for the presence of these constituents. In determining the nature of a release, it may be necessary to determine the specific waste constituents in the unit if this has not already been done. Guidance on selecting monitoring constituents is presented in Section 3 (and Appendix B); waste characterization guidance is presented in Section 7.

12.3.1.2 Physical/Chemical Properties

The physical and chemical properties of the waste constituents will affect whether they will be released, and if released, what form the release will take (i.e., vapor, particulate, or particulate-associated). These parameters are identified in Table 12-3 as a function of emission and waste type. Important parameters to consider when assessing the volatilization of a constituent include the following:

- Water solubility. The solubility in water indicates the maximum concentration at which a constituent can dissolve in water at a given temperature. This value can help the investigator estimate the

TABLE 12-3
PARAMETERS AND MEASURES FOR USE IN EVALUATING POTENTIAL RELEASES OF HAZARDOUS WASTE CONSTITUENTS TO AIR

Emission and Waste Type	Units of Concern[1/]	Useful Parameters and Measures
A. Vapor Phase Emissions		
- Dilute Aqueous Solution[2/]	Surface Impoundments, Tanks, Containers	Solubility, Vapor Pressure, Partial Pressure[3/]
- Conc. Aqueous Solution[2/]	Tanks, Containers, Surface Impoundments	Solubility, Vapor Pressure, Partial Pressure, Raoults Law
- Immiscible Liquid	Containers, Tanks	Vapor Pressure, Partial Pressure
- Solid	Landfills, Waste Piles, Land Treatment	Vapor Pressure, Partial Pressure, Octanol/Water Partition Coefficient, Porosity
B. Particulate Emissions		
- Solid	Landfills, Waste Piles, Land Treatment	Particle Size Distribution, Unit Operations, Management Methods

1/ Incinerators are not specifically listed on this table because of the unique issues concerning air emissions from these units. Although incinerators can burn many forms of waste, the potential for release from these units is primarily a function of incinerator operating conditions and emission controls, rather than waste characteristics.

2/ Although the octanol/water partition coefficient of a constituent is usually not an important characteristic in these waste streams, there are conditions where it can be critical. Specifically, in waste containing high concentrations of organic particulates, constituents with high octanol/water partition coefficients will adsorb to the particulates. They will become part of the sludge or sediment matrix, rather than volatilizing from the unit.

3/ Applicable to mixtures of volatile components.

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distribution of a constituent between the dissolved aqueous phase in the unit and the undissolved solid or immiscible liquid phase. Considered in combination with the constituent's vapor pressure, solubility can provide a relative assessment of the potential for volatilization of a constituent from an aqueous environment.

- Vapor pressure. This property is a measure of the pressure of vapor in equilibrium with a pure liquid. It is best used in a relative sense; constituents with high vapor pressures are more likely to be released than those with low vapor pressures, depending on other factors such as relative solubility and concentration (e.g., at high concentrations releases can occur even though a constituent's vapor pressure is relatively low).

- Octanol/water partition coefficient. The octanol/water partition coefficient indicates the tendency of an organic constituent to sorb to organic components of soil or waste matrices. Constituents with high octanol/water partition coefficients tend to adsorb readily to organic carbon, rather than volatilizing to the atmosphere. This is particularly important in landfills and land treatment units, where high organic carbon content in soils or cover material can significantly reduce the release potential of volatile constituents.

- Partial pressure. For constituents in a mixture, particularly in a solid matrix, the partial pressure of a constituent will be more significant than pure vapor pressure. A partial pressure measures the pressure which each component of a mixture of liquid or solid substances will exert in order to enter the gaseous phase. The rate of volatilization of an organic chemical when either dissolved in water or present in a solid mixture is characterized by the partial pressure of that chemical. In general, the greater the partial pressure, the greater the potential for release. Partial pressure values are unique for any given chemical in any given mixture and may be difficult to obtain. However when waste characterization data are available, partial pressure can be estimated using methods commonly found in engineering and environmental science handbooks.

- Henry's Law constant. Henry's law constant is the ratio of the vapor pressure of a constituent to its aqueous solubility (at equilibrium). This constant can be used to assess the relative ease with which the compound may vaporize from the aqueous phase. It is applicable only for low concentration (i.e., less than 10 percent) wastes in aqueous solution and will be most useful when the unit being assessed is a surface impoundment or tank containing dilute wastewaters. The potential for significant vaporization increases is the value for Henry's Law Constant increases; when it is greater than 10E-3, rapid volatilization will generally occur.

- Raoult's Law. Raoult's Law accurately predicts the behavior of most concentrated mixtures of water and organic solvents (i.e., solutions over 10% solute). According to Raoult's Law, the rate of volatilization of each chemical in a mixture is proportional to the product of its concentration in the mixture and its vapor pressure. Therefore, Raoult's Law can be used to characterize volatilization potential. This will be especially useful when the unit of concern entails container storage, tank storage, or treatment of concentrated waste streams.

A summary of some of these factors for several constituents is given in Tables 12-4 and 12-5. The following document contains a compilation of chemical-physical properties for several hundred constituents. Additional references for these data are provided in Section 7.

U.S. EPA. December 1987. Hazardous Waste Treatment Storage and Disposal Facilities (TSDF) - Air Emission Models. EPA-450/3-87-026. Office of Air Quality Planning and Standards. Research Triangle Park, N.C. 27711

For airborne particulates, the particle size distribution plays an important role in both dispersion and actual inhalation exposure. Large particles tend to settle out of the air more rapidly than small particles. Very small particles (i.e., those that are less than 2.5 to 10 microns in diameter) are considered to be respirable and thus present a greater health hazard than the larger particles. Therefore, the source of the release should be examined to obtain information on particle size. Process information may be sufficient to grossly characterize the potential for particulate

TABLE 12-4
PHYSICAL PARAMETERS OF VOLATILE HAZARDOUS CONSTITUENTS

Hazardous constituent	Molecular weight	Vapor pressure at 25°C (mmHg)	Solubility at 25°C (mg/l)	Henry's Law constant (atm^{-3}/mol)
Acetaldehyde	44	915	1.00E + 06	9.50E-05
Acrolein	56	244	4.00E + 05	4.07E-05
Acrylonitrile	53	114	7.90E + 04	8.80E-05
Allylchloride	76.5	340		340E-01
Benzene	78	95	1.78E + 03	5.50E-03
Benzyl chloride	126.6	1.21	1.00	
Carbon tetrachloride	154	109	8.00E + 02	2.00E-02
Chlorobenzene	112	12	5.00E + 02	2.00E-03
Chloroform	119	192	8.00E + 03	3.00E-03
Chloroprene	88.5	215		
Cresols	108	0.4	2.00E + 04	4.60E-07
Cumene (isopropylbenzene)	120	4.6	50.0	2.00E-04
1,4-dichlorobenzene	147	1.4	49.00	
1,2-dichloroethane	99	62	8.69E + 03	1.00E-04
Dichloromethane	85	360	2.00E + 04	2.00E-03
Dioxin	178	7.6E-7	3.17E-04	1.20E-03
Epichlorohydrin	92.5	13	6.00E + 04	3.08E-05
Ethylbenzene	106	10	152	7.00E-03
Ethylene oxide	44	1,095	1.35E + 05	
Formaldehyde	30	3,500	3.00E + 05	
Hexachlorobutadiene	261	0.15		
Hydrogen cyanide	27	726		
Hydrogen flouride	20	900		
Hydrogen sulfide	34	15,200		
Hexachlorocyclopentadiene	273	0.03		
Maleic anhydride	98	0.3	1.63E + 05	
Methyl acetate	74	170	3.19E + 05	1.00E-04
N-Dimethylnitrosamine	81	3.4		
Naphthlene	123	0.23		
Nitrobenzene		0.3	1.90E + 03	1.30E-05
Nitrosomorpholine		5.3		
Phenol	94	0.34	9.30E + 04	1.02E-05
Phosgene	98	1,300		
Phthalic anhydride	148	0.03	6.17E + 03	9.00E-07
Propylene oxide		400		
1,1,2,2-tetrachloroethane	168	9	2.90E + 03	2.00E-04
Tetrachloroethylene	166	15	200	
Toluene	92	30	534	5.00E-03
1,1,1-trichloroethane	133	123	720	2.15E-02
Trichloroethylene	131	90	1.10E + 03	8.92E-03
Vinylchloride	62.5	2,600	6.00E + 03	1.90E-01
Vinylidenechloride	97	500		
Xylenes	106	8.5	1.00	4.04E-04

TABLE 12-5
PHYSICAL PARAMETERS OF PCB MIXTURES*

Arochlor (PCB)	Vapor pressure at 25°C (atm)	Solubility at 25°C (mg/l)	Henry's Law constant (atm-m3/mol)
1242	2.19E-07	2400	238E-08
1248	1.02E-07	520	1.02E-08
1254	1.85E-08	120	1.40E-08
1260	5.17E-09	30	6.46E-08

* All values estimated based on calculations.

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formation. For example, the presence of ash materials and similar wastes would be a case in which particulate emissions would be of concern.

12.3.2 Unit Characterization

Different types of units may have differing release potentials. The particular type of unit, its configuration, and its operating conditions will have a great effect on the nature, extent, and rate of the release. These practices or parameters should be determined and reasonable worst-case operating practices or conditions should also be identified prior to initial sampling.

12.3.2.1 Type of Unit

The type of unit will affect its release potential and the types of releases expected. For the purpose of this guidance, units have been divided into three general types with regard to investigating releases to air. These are:

- Area sources having solid surfaces, including land treatment facilities, surfaces of landfills, and waste piles;
- Point sources, including vents, (e.g., breathing vents from tanks) and ventilation outlets from enclosed units (e.g., container handling facilities or stacks); and
- Area sources having liquid surfaces, including surface impoundments and open-top tanks.

The following discussion provides examples for each of these unit types and illustrates the kind of data that should be collected prior to establishing a sampling plan. Table 12-6 indicates types of releases most likely to be observed from each of these example unit types. It should also be recognized that releases to air can be continuous or intermittent in nature.

Waste piles--Waste piles are primary sources of particulate releases due to entrainment into the air of solid particles from the pile. Waste piles are generally comprised of dry materials which may be released into the air by wind or

TABLE 12-6
SUMMARY OF TYPICAL UNIT SOURCE TYPE AND AIR RELEASE TYPE

Typical Unit Type	Source Type			Potential Phase of Release	
	Area Sources with Liquid Surface	Area Sources with Solid Surface	Point Sources	Vapor	Particulate
Waste Piles		X		X	X
Land Treatment Units		X		X	X
Landfills		X	X	X	X
Drum Handling Facilities			X	X	X
Tanks	X		X	X	
Surface Impoundments	X			X	
Incinerators*			X	X	X

* Includes units (e.g., garbage incinerators) not covered by 40 CFR Part 264, Subpart O which pertains to hazardous waste incinerators.

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operational activities. The major air contaminants of concern from waste piles will be those compounds that are part of or have been adsorbed onto the particulates. Additionally, volatilization of some constituents may occur. Important unit factors include the waste pile dimensions (e.g., length, width, height, diameter and shape), and the waste management practices (e.g., the frequency and manner in which the wastes are applied to the pile and whether any dust suppression procedures are employed). The pile dimensions determine the surface area available for wind erosion. Disturbances to the pile can break down the surface crust and thus increase the potential for particulate emissions. Dust suppression activities, however, can help to reduce particulate emissions.

Land treatment units--Liquid or sludge wastes may be applied to tracts of soil in various ways such as surface spreading of sludges, liquid spraying on the surface, and subsurface liquid injection. These methods may also involve cultivation or tilling of the soil. Vapor phase and particulate contaminant releases are influenced by the various application techniques. Particulate or volatile emission releases are most likely to occur during initial application or during tilling, because tilling keeps the soil unconsolidated and loose, and increases the air to waste surface area.

Important unit factors in assessing an air release from a land treatment unit include:

- Waste application method - Liquid spraying applications tend to minimize particulate releases while increasing potential volatile releases. Subsurface applications generally reduce the potential for particulate and volatile releases.

- Moisture content of the waste - Wastes with high moisture content will be less likely to be released as particulates; however, a potential vapor phase release may become more likely.

- Soil characteristics - Certain constituents, such as hydrophobic organics, will be more likely to be bound to highly organic soils than non-organic soils. Therefore, releases of these types of constituents are most likely to be associated with particulate emissions.

Landfills--Landfills can result in particulate and vapor phase releases. This process generally involves placement of waste in subsurface disposal cells and subsequent covering of the waste with uncontaminated soil. Landfill characteristics that can affect contaminant release include:

- Porosity and moisture content of the soil or clay covering can influence the rate at which vapor phase releases move through the soil towards the surface. Finer soils with lower porosities will generally slow movement of vapors through the unit. The frequency of applying soil cover to the open working face of a landfill will also affect the time of waste exposure to the air.

- Co-disposal of hazardous and municipal wastes will often increase the potential for vapor phase releases, because biodegradation of municipal wastes results in the formation of methane gas as well as other volatile organics. Methane gas may act as a driving force for release of other volatile hazardous components that may be in the unit (See Section 11 - Subsurface Gas.)

- Landfill gas vents, if present, can act as sources of vapor phase emissions of contaminated landfill gases.

- Leachate collection systems can be sites of increased vapor phase emissions due to the concentrated nature of the leachate collected. Open trenches are more likely to be emission sources than underground collection sumps due to the increased exposure to the atmosphere.

- Waste mixing or consolidation areas where bulk wastes are mixed with soil or other materials (e.g., fly ash) prior to landfilling can be contributors to both particulate and vapor phase air releases. Practices such as spreading materials on the ground to release moisture prior to landfilling will also increase exposure to the atmosphere.

Drum handling facilities--Emissions from drum or container handling areas can result from several types of basic operations. Frequently, emissions from these operations are vented to the air through ducts or ventilation systems. Air sampling

to assess emissions from these operations may include sampling of the control device outlets, the workplace atmosphere at each operation, or the ambient air downwind of the unit. Factors which effect emissions include:

- Filling operations can be a major source of either vapor or particulate emissions due to agitation of the materials during the filling process. Spillage which occurs during loading may also contribute to emissions. Organic waste components with high volatility will readily vaporize into the air. Similarly, particulate matter can be atmospherically entrained by agitation and wind action. The emission potential of filling operations will be affected by exposure to ambient air. Generally, fugitive emissions from an enclosed building will be less than emissions created during loading in an open structure.

- Cleaning operations can have a high potential for emissions. These emissions may be enhanced by the use of solvents or steam cleaning equipment. The waste collection systems at these operations usually provide for surface runoff to open or below ground sumps, which can also contribute to air emissions.

- Volatilization of waste components can also occur at storage units. Since it is common practice to segregate incompatible wastes during storage, the potential for air releases may differ within a storage unit depending on the nature of the wastes stored in any particular area. The most common source of air emission releases from drum storage areas is spills from drums ruptured during shipping and handling.

- For offsite facilities, storage areas frequently are located where drums are sampled during the waste testing/acceptance process. This process involves drum opening for sampling and could also include spillage of waste materials on the ground or floor.

Important release information includes emission rates, and data to estimate release rise (e.g., vent height and diameter as well as vent exit temperature and velocity). Information pertaining to building dimension/orientation of the unit and nearby structures is needed to assess the potential for aerodynamic behavior of the

stack/vent release. These input data would be needed if atmospheric dispersion modeling was necessary.

Tanks--Tanks can emit volatile waste components under various circumstances. A major determinant of any air emission will be the type of tank being studied. Closed or fixed roof storage tanks will most likely exhibit less potential for air emissions than open topped tanks. Some tanks are equipped with vapor recovery systems that are designed to reduce emissions. Important process variables for understanding air emissions from tanks can be classified as descriptive and operational variables:

- Descriptive variables include type, age, location, and configuration of the tank.

- Operational variables include aeration, agitation, filling techniques, surface area, throughput, operating pressure and temperature, sludge removal technique and frequency, cleaning technique and frequency, waste retention and vent pipe dimensions and flow rate.

Important release information includes emission rates, and data to estimate plume rise (e.g., height and diameter as well as exit temperature and velocity). Information pertaining to building dimensions/orientation of the unit and nearby structures is needed to assess the potential for aerodynamic behavior of the stack/vent release. These input data would be needed if atmospheric dispersion modeling was necessary.

Surface impoundments--Surface impoundments are similar in many ways to tanks in the manner in which air emissions may be created. Surface impoundments are generally larger, at least in terms of exposed surface areas, and are generally open to the atmosphere. The process variables important for the evaluation of releases to air from surface impoundments can also be classified as descriptive and operational.

- Descriptive parameters include dimensions, including length, width, and depth, berm design, construction and liner materials used, and the location of the unit on the site.

- Operational parameters include freeboard, filling techniques (in particular, splash versus submerged inlet), depth of liquid and sludge layers, presence of multiple liquid layers, operating temperature, sludge removal techniques and frequency, cleaning technique and frequency, presence of aerators or mixers, biological activity factors for biotreatment, and the presence of baffles, oil layers, or other control measures on the liquid surface. (These factors are relevant to some tanks as well.)

Some surface impoundments are equipped with leak collection systems that collect leaking liquids, usually into a sump. Air emissions can also occur from these sumps. Sump operational characteristics and dimensions should be documented and, if leaks occur, the volume of material entering the sump should be documented. (These factors are relevant to some tanks as well.)

Incinerators - Stack emissions from incinerators (i.e., incinerator units not addressed by RCRA in Part 264, Subpart O, e.g., municipal refuse incinerators) can contain both particulates and volatile constituents. The high temperatures of the incineration process can also cause volatilization of low vapor pressure organics and metals. Additional volatile releases can occur from malfunctioning valves during incinerator charging. The potential for air emissions from these units is primarily a function of incinerator operating conditions and emission controls. Important unit release information includes emission rates, and data to estimate plume rise (e.g., height and diameter as well as exit temperature and velocity), as well as building dimensions/orientation of the unit and nearby structures. This information is needed to assess the aerodynamic behavior of the stack/vent release and for input to atmospheric dispersion models.

12.3.2.2 Size of Unit

The size of the unit(s) of concern will have an important impact on the potential magnitude of a release to air. The release of hazardous constituents to the air from an area source is often directly proportional to the surface area of the unit, whether this surface area is a liquid (e.g., in a tank) or a solid surface (e.g., a land treatment unit). The scope of the air investigation may be a function of the

size of the unit. Generally, more sampling locations will be required as the unit increases in size, due primarily to increased surface area. Also, as the total amount of waste material present in a particular unit increases, it will represent a larger potential reservoir or source of constituents which may be released.

Scaling factors, such as surface area to volume ratios should also be evaluated. One large waste pile, for instance, can exhibit a lower ratio of surface area to total volume than the sum of two smaller piles in which the total volume equals that of the larger pile. Other units such as tanks may exhibit a similar economy of surface area, based on the compact geometry of the unit.

Because releases to air generally occur at the waste/atmosphere interface, surface area is generally a more important factor than total waste volume. Consequently, operations that increase the atmosphere/waste interface, such as agitation or aeration, splash filling, dumping or filling operations, and spreading operations will tend to increase the emission rate. Total emissions, however, will be a function of the total mass of the waste constituent(s) and the duration of the release.

For point sources, the process or waste throughput rate will be the most important unit information needed to evaluate the potential for air emissions (i.e., stack/vent releases).

12.3.2.3 Control Devices

The presence of air pollution control devices on units can have a major influence on the nature and extent of releases. Control devices can include wet or dry scrubbers, electrostatic precipitators, baghouses, filter systems, wetting practices for solid materials, oil layers on surface impoundments, charcoal or resin absorption systems, vapor flares, and vapor recovery systems. Many of these controls systems can be installed on many of the unit types discussed in this section. Due to the variety of types of devices and the range of operational differences, an in depth discussion of individual control devices is not presented here. Additional information on control technologies for hazardous air pollutants is available in the following references:

U.S. EPA. 1986. Handbook - Control Technologies for Hazardous Air Pollutants. EPA/625/6-86/014. Office of Research and Development. Research Triangle Park, N.C. 27711.

U.S. EPA. 1986. Evaluation of Control Technologies for Hazardous Air Pollutants: Volume 1 - Technical Report. EPA/600/7-86/009a. NTIS PB 86-167020. Volume 2 - Appendices. EPA/600/7-86/009b. NTIS PB 86-167038. Office of Research and Development. Research Triangle Park, N.C. 27711.

If a control device is present on the unit of concern, descriptive and operational characteristics of the unit/control device combination should be reviewed and documented. In many cases, performance testing of these devices has been conducted after their installation on the unit(s). Information from this testing may help to quantify releases to air from the unit(s); however, this testing may not have been performed under a "reasonable worst-case" situation. The conditions under which the testing was performed should be documented.

12.3.2.4 Operational Schedules

Another characteristic which can affect the magnitude of a release to air from a unit is the unit's operational schedule. If the unit is operational on a part time or batch basis, the emission or release rate should be measured during both operational and non-operational periods. In contrast to batch operations, emission or release rates from continuous waste management operations may be measured at any time.

12.3.2.5 Temperature of Operation

Phase changes of liquids and solids to gases is directly related to temperature. Therefore, vapor phase releases to air are directly proportional to process temperature. Thus, it is important to document operational temperature (i.e., waste temperature) and fluctuations to enhance the understanding of releases to air from units. Particular attention should be paid to this parameter in the review of existing data or information regarding the operation of the unit.

The release rate of volatile components also generally increases with temperature. Frequently, the same effect is observed for particulates, because entrainment is enhanced as materials are dried. Thus, the evaporation of any water from solids, which generally increases as temperature increases, will likely increase the emissions of many particulates in the waste streams. Evaporation of water may also serve to concentrate wastes, leading to conditions more conducive to vapor phase releases to air. It should also be noted that the destruction efficiency of incinerators is also a function of temperature (i.e., higher temperatures are generally associated with greater destruction efficiency).

12.3.3 Characterization of the Environmental Setting

Environmental factors can influence not only the rate of a release to air but also the potential for exposure. Significant environmental factors include climate, soil conditions, terrain and location of receptors. These factors are discussed below.

12.3.3.1 Climate

Wind, atmospheric stability and temperature conditions affect emission rates from area sources as well as atmospheric dispersion conditions for both area and point sources. Historical summaries of climatic factors can provide a basis to assess the long-term potential for air emissions and to characterize long-term ambient concentration patterns for the area. Short-term measurements of these conditions during air monitoring will provide the meteorological data needed to interpret the concurrent air quality data. Meteorological monitoring procedures are discussed in Section 12.8. Available climatic information, on an annual and monthly or seasonal basis, should be collected for the following parameters:

- Wind direction and roses (which affects atmospheric transport, and can be used to determine the direction and dispersion of release migration);
- Mean wind speeds (which affects the potential for dilution of releases to air);
- Atmospheric stability distributions (which affects dispersion conditions);

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- Temperature means and extremes (which affects the potential for volatilization, release rise and wind erosion);

- Precipitation means (which affects the potential for wind erosion of particulates);

- Atmospheric pressure means (which affects the potential for air emissions from landfills); and

- Humidity means (which can affect the air collection efficiencies of some adsorbents - see Section 12.8).

The primary source of climate information for the United States is the National Climatic Data Center (Asheville, NC). The National Climatic Data Center can provide climate summaries for the National Weather Service station nearest to the site of interest. Standard references for climatic information include the following:

National Climatic Data Center. Local Climatological Data - Annual Summaries with Comparative Data, published annually. Asheville, NC 28801.

National Climatic Data Center. Climates of the States. 1973. Asheville, NC 28801.

National Climatic Data Center. Weather Atlas of the United States. 1968. Asheville, NC 28801.

The climatological data should be evaluated considering the effects of topography and other local influences that can affect data representativeness.

A meteorological monitoring survey may be conducted prior to ambient air monitoring to establish the local wind flow patterns and for determining the number and locations of sampling stations. The survey results will be used to characterize local prevailing winds and diurnal wind flow patterns (e.g., daytime upslope winds, nighttime downslope winds, sea breeze conditions) at the site. The survey should be conducted for a one-month period and possibly longer to adequately characterize anticipated wind patterns during the air monitoring

program. Inland, flat terrain conditions may not necessitate an onsite meteorological monitoring survey if representative data are available from previous onsite studies or from National Weather Service stations.

The meteorological monitoring data collected during the initial monitoring phase can serve as a basis for the placement of air sampling stations during any subsequent monitoring phases.

12.3.3.2 Soil Conditions

Soil conditions (e.g., soil porosity) can affect air emissions from landfills and the particulate wind erosion potential for contaminated surface soils. Soil conditions pertinent to characterizing the potential for air emissions include the following:

- Soil porosity (which affects the rate of potential gaseous emissions);
- Particle size distribution (which affects the potential for particulate emissions from contaminated soils); and
- Contaminant concentrations in soil (i.e., potential to act as air emission sources).

Soil characterization information is presented in Section 9.

12.3.3.3 Terrain

Terrain features can significantly influence the atmospheric transport of air emissions. Terrain heights relative to release heights will affect groundlevel concentration. Terrain obstacles such as hills and mountains can divert regional winds. Likewise, valleys can channel wind flows and also limit horizontal dispersion. In addition, complex terrain can result in the development of local diurnal wind circulations and affect wind speed, atmospheric turbulence and stability conditions. Topographic maps of the facility and adjacent areas are needed to assess local and regional terrain. Guidance on the appropriate format and sources of topographic and other maps is presented in Section 7 and Appendix A.

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12.3.3.4 Receptors

Information concerning the locations of nearby buildings and the population distribution in the vicinity of the site are needed to identify potential air-pathway receptors. This receptor information provides a basis for determining the need for interim corrective measures. Both environmental and human receptor information is needed to assess potential air-pathway exposures. Such information may include:

- A site boundary map;
- Location of nearest buildings and residences for each of the sixteen 22.5 degree sectors which corresponds to major compass points (e.g., north, north-northwest);
- Location of buildings and residences that correspond to the area of maximum offsite groundlevel concentrations based on preliminary modeling estimates (these locations may not necessarily be near the site boundary for elevated releases); and
- Identification of nearby sensitive receptors (e.g., nursing homes, hospitals, schools, critical habitat of endangered or threatened species).

The above information should be considered in the planning of an air monitoring program. Additional guidance on receptor information is provided in Section 2.

12.3.4 Review of Existing Information

The review of existing air modeling/monitoring data entails both summarizing the reported air contaminant concentrations as well as evaluating the quality of these data. Air data can be of many varieties and of varying utility to the RFI process. Modeling data should be evaluated based on the applicability of the model used, model accuracy, as well as the quality and representativeness of the input data.

One of the most basic parameters to review in any type of air monitoring data should be the validity of the sampling locations used during the collection of the monitoring data. The results of previous investigations should be assessed with respect to the upwind-downwind pattern around the unit to determine the likelihood that the sampling devices would have measured releases from the unit of concern. For relatively simple sites (e.g., flat terrain, constant wind speed and direction), this determination should be fairly straight-forward; however, for complex sites (e.g., complex terrain, variable winds, multiple sources, etc.), assessing the appropriateness of past sampling locations should consider such factors as potential interferences that may not have been addressed by the sampling scheme.

The most useful monitoring data are compound-specific results which can be associated with the unit being investigated, or, for point sources (such as vent stacks or ventilation system outlets), direct measurements of the exhaust prior to its release into the atmosphere. Because the hazardous properties and health and environmental criteria are compound-specific, general compound category or class data (e.g., hydrocarbon results) are less meaningful. Any existing air data should also be described and documented as to the sampling and analysis methods utilized, the associated detection limits, precision and accuracy, and the results of QA/QC analyses conducted. Results reported as non-detected (i.e., not providing numerical detection limits) are likely to be of no value.

In addition, available upwind and downwind air data should be evaluated to determine if the contamination is due to releases from the unit. If background data are available for the unit of concern, the data will be of much greater use in the planning of additional air monitoring tasks. Upwind data (to characterize ambient air background levels) are important for evaluating if downwind contamination can be attributed to the unit of concern. If background data are not available, the existing downwind air concentration data will be of less value in characterizing a release; however, the lack of background data does not negate the utility of the available monitoring data.

Data may also be available from air monitoring studies that did not focus directly on releases from a unit of concern. Many facilities conduct onsite health and safety programs, including routine monitoring of air quality for purposes of evaluating worker exposure. This type of data may include personnel hygiene

monitoring results from personal sampling systems worn by employees as they perform their jobs, general area monitoring of zones at which hazardous operations are conducted, or actual unit-emission monitoring. The detection limits of these methods (generally in parts per million) are frequently higher than are needed for RFI purposes. However, this type of industrial hygiene monitoring is frequently compound-specific, and can be useful in qualitatively evaluating the air emissions from particular sources.

Indoor air monitoring, generally only applicable to units that are enclosed in a building (e.g., drum handling areas or tanks), often includes flow monitoring of the ventilation system. Monitoring of hoods and ductwork systems may have been conducted to determine exchange time and air circulation rates. These flow determinations could prove to be useful in the evaluation of air emission measurements during the RFI.

Another important aspect of the existing data review is to document any changes in composition of the waste managed in the unit of concern since the air data were collected. Also, changes in operating conditions or system configuration for waste generation and/or unit functions could have major effects on the nature or extent of releases to air. If such operational or waste changes have occurred, they should be summarized and reviewed to determine their role in the evaluation of existing data. This summary and review will not negate the need to take new samples to characterize releases from the unit. However, such information can be useful in the planning of the new air monitoring activities.

12.3.5 Determination of "Reasonable Worst-Case" Exposure Period

A "reasonable worst-case" exposure period over a 90 day period should be identified if an air monitoring program is to be conducted. Determination of reasonable worst-case exposure conditions will aid in planning the air monitoring program and is dependent on seasonal variations in emission rates and dispersion conditions.

The selection of the "reasonable worst-case" 90-day exposure period for the conduct of air monitoring should account for the following factors:

- For vapor phase releases, wind speed and temperature are the key factors affecting releases from the unit. In general, the higher the temperature and windspeed, the greater the rate of volatilization of constituents of concern from the waste. This process is tempered, however, by the fact that at higher windspeeds, dispersion of the release is generally greater, resulting in lower downwind concentrations at potential exposure points.

- For particulate releases, wind speed is the key meteorological factor. The amount of local precipitation contributing to the degree of moisture of the waste may also be important. In general, the higher the windspeed, and the drier the waste, the greater will be the potential for particulate release. As with vapor phase releases, higher wind speeds may also lead to greater dispersion of the release, resulting in lower downwind concentrations.

- For point source releases, increased wind speeds and unstable atmospheric conditions (e.g., during cloudless days) enhance dispersion but also tend to reduce plume height and can lead to relatively high groundlevel concentrations.

- Constituent concentrations at any downwind sector will also be directly affected by the wind direction and frequency.

Air emission release rate models and atmospheric dispersion models can be used to identify reasonable worst-case exposure conditions (i.e., to quantitatively account for the above factors). For this application, it is recommended that the modeling effort be limited to a screening/sensitivity exercise with the objective of obtaining "relative" results for a variety of source and meteorological scenarios. By comparing results in a relative fashion, only those input meteorological parameters of greatest significance (e.g., temperature, wind speed and stability) need to be considered.

In general, the summer season will be the "reasonable worst-case" exposure period at most sites because of relatively high temperatures and low windspeeds. Spring and fall are also candidate monitoring seasons that should be evaluated on a

site-specific basis. Winter is generally not a prime season for air monitoring due to lower temperatures and higher wind speeds.

12.4 Air Emission Modeling

12.4.1 Modeling Applications

Air emission models can be used to estimate constituent-specific emission rates based on waste/unit input data for many types of waste management units. (An emission rate is defined as the source release rate for the air pathway in terms of mass per unit of time.)

An important application of emission models in the RFI release characterization strategy for air is the conduct of screening assessments. For this application, available waste/unit input data for emission models, in conjunction with dispersion modeling results, are used to estimate concentrations at locations of interest. These results can then be evaluated to determine if adequate information is available for RFI decisionmaking or if monitoring is needed to further reduce the uncertainty associated with characterizing the release. Depending on the degree of uncertainty in the estimated concentrations relative to the differences between the estimated concentrations and the health based levels, modeling results may be sufficient to characterize the release as significant (i.e., implementation of corrective action would be appropriate) or as insignificant (i.e., no further action is warranted).

Emission rate models can also be used to identify potential major air emission sources at a facility (especially multiple-unit facilities). For this type of application, modeling results are used to compare routine long-term emissions from various units to prioritize the need for release characterization at each unit. For example, modeling results may indicate that 90 percent of the volatile organic compound emissions at a facility are attributable to surface impoundment units and only 10 percent to other sources. Therefore, emphasis should be on characterizing releases from the surface impoundments.

Emission modeling is not available for all air-related phenomenon associated with waste management. For example, anaerobic biological activity in surface

impoundments may, in certain instances, contribute to air pollution by emitting constituents not contained in the waste placed in the impoundment and which available models do not adequately address. In such instances, source testing or monitoring may be necessary; based on such monitoring, emission rates can be developed.

12.4.2 Model Selection

The information gathered during the initial stage of the air investigation should be used to select appropriate models and to estimate unit-specific and constituent-specific emission rates. A thorough understanding of the available models is needed before selecting a model for an atypical emission source. When gathering information on any emission source, it would be useful to obtain a perspective of the potential variability of the waste and unit input data. A sensitivity analysis of this variability relevant to emission rate estimates would help determine the level of confidence associated with the emission modeling results.

Air emission models can be classified into two categories; models which can be used to estimate volatile organic releases, and models which can be used to estimate particulate emissions. These are discussed below.

12.4.2.1 Organic Emissions

Comprehensive guidance on the application of air emission models for volatile organic releases from various units is presented in the following references:

U.S. EPA. December 1987. Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF) - Air Emission Models. EPA-450/3-87-026. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

U.S. EPA. December 1988 Draft. Procedures for Conducting Air Pathway Analyses for Superfund Applications. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

These references provide modeling guidance for the following units:

- Surface impoundments
  - Storage impoundments
  - Disposal impoundments
  - Mechanically aerated impoundments
  - Diffused air systems
  - Oil film surfaces

- Land treatment
  - Waste application
  - Oil film surfaces
  - Tilling

- Landfills
  - Closed landfills
  - Fixation pits
  - Open landfills

- Waste piles

- Transfer, storage and handling operations
  - Container loading
  - Container storage
  - Container cleaning
  - Stationary tank loading
  - Stationary tank storage
  - Spills
  - Fugitive emissions
  - Vacuum truck loading

Emission factors for various evaporation loss sources (e.g., storage and handling of organic liquids) are provided in the following reference:

U.S. EPA. 1985. (Fourth edition and subsequent supplements) Compilation of Air Pollutant Emission Factors. EPA AP-42. NTIS PB 86-124906. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

An emission factor is generally defined as an average value which relates the quantity of a pollutant released to the atmosphere with the activity associated with the release of the pollutant. However, for estimation of organic releases from storage tanks, the emission factors are presented in terms of empirical formulae which can relate emissions to such variables as tank diameter, liquid temperature, etc.

Selection of an appropriate air emission model will be based primarily on selection of a model which is appropriate for the unit of concern, has technical credibility and is practical to use. Some of the models presented in Hazardous Waste Treatment, Storage and Disposal Facilities (TSDF) - Air Emission Models (U.S. EPA, December 1987), are available on a diskette for use on a microcomputer. Computer-compatible air emission models (referred to as CHEMDAT6 models) are available for the following sources.

- Nonaerated impoundments
- Open tanks
- Aerated impoundments
- Land treatment
- Landfills

These models are prime candidates for RFI air release characterization applications.

12.4.2.2 Particulate Emissions

Guidance on the selection and application of air emission models for particulate releases is presented in the following references:

U.S. EPA. February 1985. Rapid Assessment of Exposure to Particulate Emissions from Surface Contamination Sites. EPA/600-18-85/002. Office of Health and Environmental Research. Washington, D.C. 20460.

U.S. EPA. 1985. (Fourth edition and subsequent supplements) Compilation of Air Pollutant Emission Factors. EPA, AP-42. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

U.S. EPA. 1978. Fugitive Emissions from Integrated Iron and Steel Plants. EPA 600/2-78-050. Washington, D.C. 20460.

U.S. EPA. December 1988 Draft. Procedures for Conducting Air Pathway Analysis for Superfund Applications. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

These references provide modeling guidance for the following particulate sources and associated operations and activities (e.g., vehicular traffic):

- Wastepiles
- Flat, open surfaces

The air emission models for both types of sources should account for both wind erosion potential as well as releases due to mechanical disturbances.

The U.S. EPA-Office of Air Quality Planning and Standards is currently developing guidance regarding particulate emissions from hazardous waste transfer, storage and disposal facilities.

12.4.3 General Modeling Considerations

Organics in surface impoundments, land treatment facilities, landfills, and wastepiles, can depart through a variety of pathways, including volatilization, biological decomposition, adsorption, photochemical reaction, and hydrolysis. To allow reasonable estimates of organic disappearance, it is necessary to determine which pathways predominate for a given chemical, type of unit, and set of meteorological conditions.

Source variability will significantly influence the relative importance of the pathways. For highly variable sources it may be possible to exclude insignificantly small pathways from consideration. The relative magnitude of these pathways then

can be computed by applying the methodology to a model facility to determine relative differences among various compounds. A summary of typical pathways for air emission sources is presented in Table 12-7.

It is also necessary to consider the variation of waste composition as a function of time as well as other potential variations in source conditions. These variable conditions may necessitate multiple modeling scenarios to adequately characterize representative waste/unit conditions.

12.5 Dispersion Modeling

12.5.1 Modeling Applications

Atmospheric dispersion models can be used to estimate constituent-specific concentrations at locations of interest based on input emission rate and meteorological input data. The major RFI dispersion modeling applications for characterizing releases to air can be summarized as follows:

- Screening assessments: Dispersion models can be used to estimate concentrations at locations of interest using input emission rate data based on air emission modeling.

- Emission monitoring: Dispersion models can be used to estimate concentrations at locations of interest using input emission rate data based on emission rate monitoring.

- Confirmatory air monitoring: Dispersion modeling can be used to assist in designing an air monitoring program (i.e., to determine appropriate monitoring locations and monitoring period) as well as for interpretation and extrapolation of monitoring results.

Atmospheric dispersion models can be used for monitoring program design applications to identify areas of high concentration relative to the facility property boundary or actual receptor locations. High concentration areas which correspond to actual receptors are priority locations for air monitoring stations.

TABLE 12-7

TYPICAL PATHWAYS FOR AREA EMISSION SOURCES[a]

Pathway	Surface Impoundments	Land Treatment	Landfill
Volatilization	I	I	I
Biodegradation	I	I	S
Photodecomposition	S	N	N
Hydrolysis	S	N	N
Oxidation/reduction	N	N	N
Adsorption	N	N	N
Hydroxyl radical reaction	N	N	N
Migration[b]	N	N	N
Runoff[b]	N	N	N

I = Important
S = Secondary
N = Negligible or not applicable

a Individual chemicals in a given site type may have dominant pathways different from the ones shown here.

b Water migration and runoff are considered to have negligible effects on ground and surface water in a properly sited, operated, and maintained RCRA-permitted hazardous waste treatment, storage, and disposal facility.

Dispersion models (with input emission rates based on emission models) can also be used to provide seasonal air concentration "patterns" based on available representative historical meteorological data (either onsite or offsite). Comparison of seasonal air concentration patterns can be used to identify the "reasonable worst case" period for monitoring. Air concentration patterns based on modeling results can similarly be used to evaluate the representativeness of the actual data collection period. Representativeness is determined by comparing the air concentration patterns for the actual air monitoring period with historic seasonal air concentration patterns.

The objective of the modeling applications discussed above involves the estimation of long-term (i.e., several months to years) concentration patterns. These long-term patterns do not have the variability associated with short-term (i.e., hours to days, such as a 24-hour event) emission rate and dispersion conditions, and are more conducive to data extrapolation applications. For example, near source and fenceline air monitoring results can be used to back calculate an emission rate for the source. This estimated emission rate can be used as dispersion modeling input to estimate offsite air concentrations for the same downwind sector and exposure period as for the air monitoring period.

12.5.2 Model Selection

Guidance on the selection and application of dispersion models is provided in the following references:

U.S. EPA. July 1986. Guidelines on Air Quality Models (Revised). EPA-450/12-78-027R. NTIS PB86-245248. Office of Air Quality Planning and Standards. Research Triangle Part, NC 27711.

U.S. EPA. December 1988 Draft. Procedures for Conducting Air Pathway Analyses for Superfund Applications. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

The following information is based primarily on guidance provided in these references.

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12.5.2.1 Suitability of Models

The extent to which a specific air quality model is suitable for the evaluation of source impact depends upon several factors. These include: (1) the meteorological and topographic complexities of the area; (2) the level of detail and accuracy needed for the analysis; (3) the technical competence of those undertaking such simulation modeling; (4) the resources available; and (5) the detail and accuracy of the data base, i.e., emissions inventory, meteorological data, and air quality data. Appropriate data should be available before any attempt is made to apply a model. A model that requires detailed, precise, input data should not be used when such data are unavailable. However, assuming the data are adequate, the greater the detail with which a model considers the spatial and temporal variations in emissions and meteorological conditions, the greater the ability to evaluate the source impact and to distinguish the effects of various control strategies.

Air quality models have been applied with the most accuracy or the least degree of uncertainty to simulations of long term averages in areas with relatively simple topography. Areas subject to major topographic influences experience meteorological complexities that are extremely difficult to simulate. Although models are available for such circumstances, they are frequently site-specific and resource intensive. In the absence of a model capable of simulating such complexities, only a preliminary approximation may be feasible until such time as better models and data bases become available.

Models are highly specialized tools. Competent and experienced personnel are an essential prerequisite to the successful application of simulation models. The need for specialists is critical when the more sophisticated models are used or the area being investigated has complicated meteorological or topographic features. A model applied improperly, or with inappropriately chosen data, can lead to serious misjudgments regarding the source impact or the effectiveness of a control strategy.

The resource demands generated by use of air quality models vary widely depending on the specific application. The resources required depend on the nature of the model and its complexity, the detail of the data base, the difficulty of

the application, and the amount and level of expertise required. The costs of manpower and computational facilities may also be important factors in the selection and use of a model for a specific analysis. However, it should be recognized that under some sets of physical circumstances and accuracy requirements, no present model may be appropriate. Thus, consideration of these factors should not lead to selection of an inappropriate model.

12.5.2.2 Classes of Models

Dispersion models can be categorized into four generic classes: Gaussian, numerical, statistical or empirical, and physical. Within these classes, especially Gaussian and numerical models, a large number of individual "computational algorithms" may exist, each with its own specific applications. While each of the algorithms may have the same generic basis, e.g., Gaussian, it is accepted practice to refer to them individually as models. In many cases the only real difference between models within the different classes is the degree of detail considered in the input or output data.

Gaussian models are the most widely used techniques for estimating the impact of nonreactive pollutants. Numerical models may be more appropriate than Gaussian models for area source urban applications that involve reactive pollutants, but they require much more extensive input data bases and resources and therefore are not as widely applied. Statistical or empirical techniques are frequently employed in situations where incomplete scientific understanding of the physical and chemical processes or lack of the required data bases make the use of a Gaussian or numerical model impractical.

Physical modeling, the fourth generic type, involves the use of wind tunnel or other fluid modeling facilities. This class of modeling is a complex process requiring a high level of technical expertise, as well as access to the necessary facilities. Nevertheless, physical modeling may be useful for complex flow situations, such as building, terrain or stack down-wash conditions, plume impact on elevated terrain, diffusion in an urban environment, or diffusion in complex terrain. It is particularly applicable to such situations for a source or group of sources in a geographic area limited to a few square kilometers. The publication "Guideline for Fluid Modeling

of Atmospheric Diffusion" provides information on fluid modeling applications and the limitations of that method (U.S. EPA, 1981).

12.5.2.3 Levels of Sophistication of Models

In addition to the various classes of models, there are two levels of sophistication. The first level consists of general, relatively simple estimation techniques that provide conservative estimates of the air quality impact of a specific source, or source category. These are screening techniques or screening models. The purpose of such techniques is to eliminate the need for further more detailed modeling for those sources that clearly can be characterized and evaluated based on simple screening assessments.

The second level consists of those analytical techniques that provide more detailed treatment of physical and chemical atmospheric processes, require more detailed and precise input data, and provide more specialized concentration estimates. As a result they provide a more refined and, at least theoretically, a more accurate estimate of source impact and the effectiveness of control strategies. These are referred to as refined models.

The use of screening techniques followed by a more refined analysis is always desirable, however, there are situations where the screening techniques are practically and technically the only viable option for estimating source impact. In such cases, an attempt should be made to acquire or improve the necessary data bases and to develop appropriate analytical techniques.

12.5.2.4 Preferred Models

Guidance on EPA preferred models for screening and refined applications is provided in the following references:

U.S. EPA. July 1986. Guidelines on Air Quality Models (Revised). EPA-450/2-78-027R. NTIS PB86-245248. Office of Air Quality Planning and Standards. Research Triangle Park, N.C. 27711.

U.S. EPA. October 1977. Guidelines for Air Quality Maintenance Planning and Analysis. Vol. 10 (Revised): Procedures for Evaluating Air Quality Impact of New Stationary Sources. EPA-450/4-77-001. NTIS PB274-087. Office of Air Quality Planning and Standards. Research Triangle Park, N.C. 27711.

U.S. EPA. December 1988 Draft. Procedures for Conducting Air Pathway Analyses for Superfund Applications. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

Appropriate dispersion models commensurate with the above guidance and sutiable for mainframe computer use are included in the UNAMAP series available from NTIS. Versions of the UNAMAP models suitable for use on a microcomputer are also available from commercial sources.

Alternative screening approaches based on hand calculations are available for point sources located in flat terrain based on the following guidance:

Turner, D.B. 1969. Workbook of Atmospheric Dispersion Estimates. Public Health Service. Cincinnati, OH.

U.S. EPA. March 1988 Draft. A Workbook of Screening Techniques for Assessing Impacts of Toxic Air Pollutants. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

Preferred models for selected applications in simple terrain are identified in Table 12-8. Appropriate dispersion models for complex terrain applications generally need to be determined on a case-by-case basis. Acceptable models may not be available for many complex terrain applications.

The use of the Industrial Source Complex (ISC) Model is recommended as a prime candidate for RFI atmospheric dispersion modeling applications. Applicable ISC source types include stack area and volume sources. Concentration estimates can be based on times of as short as one hour and as long as one year. The model can be used for both flat and rolling terrain. The ISC model can also account for atmospheric deposition (i.e., inter-media transport to soil). The ISC Model (See EPA

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TABLE 12-8

PREFERRED MODELS FOR SELECTED APPLICATIONS IN SIMPLE TERRAIN

Short Term (1-24 hours)	Land Use	Model*
Single Source	Rural Urban	CRSTER RAM
Multiple Source	Rural Urban	MPTER RAM
Complicated Sources**	Rural/Urban	ISC*
Buoyant Industrial Line Sources	Rural	BLP
Long Term (monthly, seasonal or annual)		
Single Source	Rural Urban	CRSTER RAM
Multiple Source	Rural Urban	MPTER CDM 2.0 or RAM***
Complicated Sources**	Rural/Urban	ISC*
Buoyant Industrial Line Sources	Rural	BLP

* The long-term version of ISC (i.e., ISCLT) is recommended as the preferred dispersion model for RFI applications.

** Complicated sources are sources with special problems such as aerodynamic downwash, particle deposition, volume and area sources, etc.

***If only a few sources in an urban area are to be modeled, RAM should be used.

450/4-86-005a and b) is included in the UNAMAP series available through the NTIS (U.S. EPA, June 1986).

Additional guidance on dispersion model selection and application is available from EPA Regional Office and State modeling representatives as well as from the EPA Model Clearinghouse.

If other than preferred models are selected for use, early discussions with the regulatory agency is encouraged. Agreement on the data base to be used, modeling techniques to be applied and the overall technical approach, prior to the actual analyses, helps avoid misunderstandings concerning the final results and may reduce the later need for additional analyses. The preparation (and submittal to the appropriate regulatory agency) of a written modeling protocol is recommended for all RFI atmospheric dispersion modeling applications.

12.5.3 General Modeling Considerations

Dispersion modeling results are limited by the amount, quality and representativeness of the input data. In addition to meteorological and source data modeling input, the following are also important modeling factors:

- Location of facility property boundary
- Dispersion coefficients
- Stability categories
- Plume rise
- Chemical transformation
- Gravitational settling and deposition
- Urban/rural classification

In designing a computational network for modeling, the emphasis should be placed on location with respect to the facility property boundary. The selection of sites should be a case-by-case determination taking into consideration the topography, the climatology, monitor sites, and should be based on the results of the initial screening procedure. Additional locations may be needed in the high concentration location if greater resolution is indicated by terrain or source factors.

Gaussian models used in most applications should employ dispersion coefficients consistent with those contained in the preferred models available in UNAMAP. Factors such as averaging time, urban/rural surroundings, and type of source (point vs. line) may dictate the selection of specific coefficients.

The Pasquill approach to classifying stability is generally required in all preferred models. The Pasquill method, as modified by Turner, was developed for use with commonly observed meteorological data from the National Weather Service (NWS) and is based on cloud cover, insolation and wind speed.

Procedures to determine Pasquill stability categories from other than NWS data are presented in Guidelines on Air Quality Models (Revised) (U.S. EPA, July 1986). Any other method to determine Pasquill stability categories should be justified on a case-by-case basis.

The plume rise methods incorporated in the EPA preferred models are recommended for use in all modeling applications. No provisions in these models are made for fumigation or multi-stack plume rise enhancement or the handling of such special plumes as flares; these problems should be considered on a case-by-case basis.

Where aerodynamic downwash occurs due to the adverse influence of nearby structures, the algorithms included in the ISC model should be used.

Use of models incorporating complex chemical mechanisms should be considered only on a case-by-case basis with proper demonstration of applicability. These are generally regional models not designed for the evaluation of individual sources but used primarily for region-wide evaluations.

An "infinite half-life" should be used for estimates of total suspended particulate concentrations when Gaussian models containing only exponential decay terms for treating settling and deposition are used. Gravitational settling and deposition may be directly included in a model if either is a significant factor. At least one preferred model (ISC) contains settling and deposition algorithms and is recommended for use when particulate matter sources can be quantified and settling and deposition are problems.

The selection of either rural or urban dispersion coefficients in a specific application should follow one of the procedures presented in Guidelines on Air Quality Models (Revised) (U.S. EPA, July 1986). These include a land use classification procedure or a population based procedure to determine whether the character of an area is primarily urban or rural.

12.6 Design of a Monitoring Program to Characterize Releases

Monitoring procedures should be developed based on the information previously described, including determination of reasonable worst-case scenarios as discussed above. This section discusses the recommended monitoring approaches.

Primary elements in designing a monitoring system include:

- Establishing monitoring objectives;
- Determining monitoring constituents of concern;
- Monitoring schedule;
- Monitoring approach; and
- Monitoring locations.

Each of these elements should be addressed to meet the objectives of the initial monitoring phase, and any subsequent monitoring that may be necessary. These elements are described in detail below.

12.6.1 Objectives of the Monitoring Program

The primary goal of the air investigation is to determine concentrations at the facility property boundary as input to the health and environmental assessment process. As discussed previously, the monitoring program may be conducted in a phased approach, using the results of initial monitoring and/or modeling to determine the need for and scope of subsequent monitoring.

Principal components of both the initial and subsequent monitoring phases are:

- Identification or verification of constituents;

- Characterization of long-term air constituent concentrations (based on a "reasonable worst case" exposure period) at:
  - the unit boundary to maximize the potential for release detection
  - the facility property boundary
  - actual offsite receptor locations (for determining the need for interim corrective measures)
  - areas upwind of the release source (to characterize background concentrations); and

- Collection of meteorological data during the monitoring period to aid in evaluating the air monitoring data.

Atmospheric dispersion modeling may also be used to estimate concentrations, if monitoring is not practical, as discussed previously.

Subsequent monitoring may be necessary if initial monitoring and modeling data were not sufficient to characterize long-term ambient constituent concentrations.

12.6.2 Monitoring Constituents and Sampling Considerations

Sampling and analysis may be conducted for all appropriate Appendix VIII constituents that have an air pathway potential (See Section 3 and Appendix B). An alternative approach is to use unit and waste-specific information to identify constituents that are not expected to be present and thus, reduce the list of target monitoring constituents. For example, the industry specific monitoring constituent lists presented in Appendix B, List 4 can be used to identify appropriate air monitoring constituents for many applications (especially for units that serve only a limited number of industrial categories). The target constituents selected should be

limited to those which may be present in the waste and have health criteria for the air pathway (see Section 8).

Results from screening assessment, emission monitoring, and/or screening sampling phase (as defined later in Section 12.6.4.1) may also be used as a basis for selection of monitoring constituents. These results may confirm/identify appropriate monitoring constituents for the unit of concern.

12.6.3 Meteorological Monitoring

Monitoring of onsite meteorological conditions should be performed in concert with other emission rate and air monitoring activities. Meteorological monitoring results can serve as input for dispersion models, can be used to assure that the air monitoring effort is conducted during the appropriate meteorological conditions (e.g., "reasonable worst case" period for initial monitoring), and to aid in the interpretation of air monitoring data.

12.6.3.1 Meteorological Monitoring Parameters

The following meteorological parameters should be routinely monitored while collecting ambient air samples:

- Horizontal wind speed and direction;
- Ambient temperature;
- Atmospheric stability (e.g., based on the standard deviation of horizontal wind direction or alternative standard methodologies);
- Precipitation measurements if representative National Weather Service data are not available; and
- Atmospheric pressure (e.g., for landfill sites or contaminated soils) if representative National Weather Service data are not available.

It is recommended that horizontal wind speed and direction, and air temperature be determined onsite with continuous recording equipment. Estimates from offsite monitors are not likely to be representative for all of the conditions at the site. Input parameters for dispersion models, if appropriate, should be reviewed prior to conducting the meteorological data collection phase to ensure that all necessary parameters are included.

Field equipment used to collect meteorological data can range in sophistication from small, portable, battery-operated units with wind speed and direction sensors, to large, permanently mounted, multiple sensor units at varying heights. Individual sensors can collect data on horizontal wind speed and direction, three-dimensional wind speed, air temperature, humidity, dew point, and mixing height. From such data, variables for dispersion models such as wind variability and atmospheric stability can be determined. Additional guidance on meteorological measurements can be obtained from:

U.S. EPA. June 1987. On-Site Meteorological Program Guidance for Regulatory Modeling Applications. EPA-450/4-87-013. Office of Air Quality Planning and Standards. Research Triangle Park, N.C. 27711.

U.S. EPA. February 1983. Quality Assurance handbook for Air Pollution Measurements Systems: Volume IV. Meteorological Measurements. EPA-600/4-82-060. Office of Research and Development. Research Triangle Park, N.C. 27711.

U.S. EPA. July 1986. Guidelines on Air Quality Models (Revised). EPA-405/2-78-027R. NTIS PB 86-245248. Office of Air Quality Planning and Standards. Research Triangle Park, N.C. 27711.

Appropriate performance specifications for monitoring equipment are given in the following document:

U.S. EPA. November 1980. Ambient Monitoring Guidelines for Prevention of Significant Deterioration (PSD). EPA-450/4-80/012. NTIS PB 81-153231. Office of Air Quality Planning and Standards. Research Triangle Park, N.C. 27711.

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12.6.3.2 Meteorological Monitor Siting

Careful placement of meteorological monitoring equipment (e.g., sensors) is important in gathering relevant data. The objective of monitoring tower placement is to position sensors to obtain measurements representative of the conditions that determine atmospheric dispersion in the area of interest. The convention for placement of meteorological monitoring equipment is:

- At or above a height of 10 meters above ground; and
- At a horizontal distance of 10 times the obstruction height from any upwind obstructions.

In addition, the recommendations given in Table 12-9 should be followed to avoid effects of terrain on meteorological monitors.

Depending on the complexity of the terrain in the area of interest and the parameters being measured, more than one tower location may be necessary. Complex terrain can greatly influence the transport and diffusion of a contaminant release to air so that one tower may not able to account for these influences. The monitoring station height may also vary depending on source characteristics and logistics. Heights should be selected to minimize near-ground effects that are not representative of conditions in the atmospheric layer into which a constituent of concern is being released.

A tower designed specifically to mount meteorological instruments should be used. Instruments should be mounted on booms projecting horizontally out from the tower at a minimum distance of twice the tower diameter. Sound engineering practice should be used to assure tower integrity during all meteorologic conditions.

Further guidance on siting meteorological instruments and stations is available in the following publications:

TABLE 12-9

RECOMMENDED SITING CRITERIA TO AVOID TERRAIN EFFECTS

Distance from Tower (meters)	Maximum Acceptable Construction or Vegetation Height (meters)
0 - 15	0.3
15 - 30	0.5 - 1.0
30 - 100	3
100 - 300	10

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U.S. EPA. November 1980. Ambient Monitoring Guidelines for Prevention of Significant Deterioration (PSD). EPA-450/4-80-012. NTIS PB 81-153231. Office of Air Quality Planning and Standards. Research Triangle Park, N.C. 27711.

U.S. EPA. June 1987. On-Site Meteorological Program Guidance for Regulatory Modeling Applications. EPA-450/4-87-013. Office of Air Quality Planning and Standards. Research Triangle Park, N.C. 27711.

U.S. EPA. February 1983. Quality Assurance Handbook for Air Pollution Measurement Systems: Volume IV. Meteorological Measurements. EPA-600/4-82-060. Office of Research and Development. Research Triangle Park, N.C. 27711.

12.6.4 Monitoring Schedule

Establishment of a monitoring schedule is an important consideration in developing a monitoring plan. When appropriate, air monitoring should coincide with monitoring of other media (e.g., subsurface gas, soils, and surface water) that have the potential for air emissions. As with all other aspects of the monitoring program, the objectives of monitoring should be considered in establishing a schedule. As indicated previously, monitoring generally consists of screening sampling, emission monitoring, and air monitoring. The monitoring schedule during each of these phases is discussed below.

12.6.4.1 Screening Sampling

A limited screening sampling effort may be necessary to focus the design of additional monitoring phases. Therefore, screening samples may be warranted during the screening assessment or prior to initiating emission monitoring or air monitoring studies. This screening phase can also be used to supplement modeling and emission monitoring results as available, to verify the existence of a release to air, and to prioritize the major release sources at the facility.

Screening sampling should be used to characterize air emissions (e.g., by using total hydrocarbon measurements as an indicator), and to confirm/identify the presence of candidate constituents. Screening samples should generally consist of

source emissions measurements or ambient air samples collected at or in close proximity to the source. This approach will provide the best opportunity for detection of air emission constituents. (A discussion of available screening methods is presented in Section 12.8.) An alternative screening approach involves collection of a limited number of air samples to facilitate the analysis of a wide range of constituents (e.g., collection via Tenax adsorption tubes or whole air sampling with analysis by GC/MS - see Section 12.8).

The screening study should generally involve collection of a limited number of grab or time-integrated samples (several minutes to 24 hours) for a limited time period (e.g., one to five days). Sampling should be conducted during emission/dispersion conditions that are expected to result in relatively high concentrations, as discussed previously. Screening results should be interpreted considering the representativeness of the waste and unit operations during the sampling, and the detection capabilities of the screening methodology used.

12.6.4.2 Emission Monitoring

Emission rate monitoring may be necessary to characterize a release if screening assessment results are not conclusive. This approach involves stack or vent emission monitoring for point sources. Point source monitoring is not dependent on meteorological conditions. However, emission rate monitoring for both point and area sources should be conducted during typical or "reasonable worst case" emission rate conditions. Therefore, emission monitoring should be conducted when source conditions (e.g., unit operations and waste concentrations) as well as meteorological conditions are conducive to "reasonable worst case" emission rate conditions. Emission rate monitoring for area sources should not be conducted during or immediately following precipitation or if hourly average wind speeds are greater than 15 miles per hour. It should also be noted that soil or cover material (if present) should be allowed to dry prior to continuing monitoring operations, as volatilization decreases under saturated soil conditions. In these cases, the monitoring should be interrupted and resumed as soon as possible after the unfavorable conditions pass. Similarly, operational interruptions such as unit shutdown should also be factored into the source sampling schedule.

Point source emission sampling generally requires only a few hours of sampling and occurs during a more limited time (e.g., one to three days). Guidance on point-source sampling schedules is presented in the following:

U.S. EPA. November 1985. Practical Guide - Trial Burns for Hazardous Waste Incinerators. NTIS PB 86-190246. Office of Research and Development. Cincinnati, OH 45268.

U.S. EPA. Code of Federal Regulations. 40 CFR Part 60: Appendix A: Reference Methods. Office of the Federal Register. Washington, D.C.

U.S. EPA. 1978. Stack Sampling Technical Information, A Collection of Monographs and Papers, Volumes I-III. EPA-450/2-78-042a,b,c. NTIS PB 80-161672, 80-161680, 80-161698. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

U.S. EPA. February 1985. Modified Method 5 Train and Source Assessment Sampling System Operators Manual. EPA-600/8-85-003. NTIS PB 85-169878. Office of Research and Development. Research Triangle Park, NC 27711.

U.S. EPA. March 1984. Protocol for the Collection and Analysis of Volatile POHCs Using VOST. EPA-600/8-84-007. NTIS PB 84-170042. Office of Research and Development. Research Triangle Park, NC 27711.

U.S. EPA. February 1984. Sampling and Analysis Methods for Hazardous Waste Combustion. EPA-600/8-84-002. NTIS PB 84-155845. Washington, D.C. 20460.

U.S. EPA. 1981. Source Sampling and Analysis of Gaseous Pollutants. EPA-APTI Course Manual 468. Air Pollution Control Institute. Research Triangle Park, NC 27711.

U.S. EPA. 1979. Source Sampling for Particulate Pollutants. EPA-APTI Course Manual 450. NTIS PB 80-188840, 80-182439, 80-174360. Air Pollution Control Institute. Research Triangle Park, NC 27711.

U.S. EPA. 1986. Test Methods for Evaluating Solid Waste. 3rd Edition. Office of Solid Waste. EPA/SW-846. GPO No. 955-001-00000-1. Washington, D.C. 20460.

Emission rate monitoring should be conducted during a 1 to 3 day period representative of "reasonable worst case" source emission conditions. The worst case short-term emission rate conditions should be determined by parametric analyses (i.e., by modeling a wide range of source operational conditions and associated waste concentrations as well as meteorological conditions for parameters such as wind speed and temperature). Historical meteorological data representative of the site should be reviewed to determine the season and time of day associated with worst case emission conditions. These results should be used to select and schedule (along with meteorological forecasts for local conditions and expected source operational and waste concentration) the emission monitoring period.

Emission rate monitoring results based on measurements during worst-case conditions should be initially used as dispersion modeling input. If these initial results exceed health criteria then the emission monitoring results should be scaled to represent long term (i.e., annual) conditions. The scaling factor should be based on the ratio of emission rate modeling results (using meteorological conditions during the monitoring period as input) compared to modeling results based on typical (annual) meteorological conditions.

Guidance on area source emission rate monitoring is provided in the following:

U.S. EPA. 1986. Measurement of Gaseous Emission Rates from Land Surfaces Using an Emission Isolation Flux Chamber: User's Guide. EPA/600/8-86/008. NTIS PB86-223161. Environmental Monitoring Systems Laboratory. Las Vegas, NV 89114.

U.S. EPA. December 1988 Draft. Procedures for Conducting Air Pathway Analyses for Superfund Applications. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

12.6.4.3 Air Monitoring

The primary objective of confirmatory monitoring is to characterize long-term exposures that may be associated with air emissions from the unit under reasonable worst-case conditions. A schedule should be proposed that will provide an adequate degree of confidence that those compounds that may be released will be detected (i.e., by sampling during the season associated with the highest air concentrations as determined based on modeling). Laboratory analytical costs typically range from $200 to over $1,000 per air monitoring station for one 24-hour integrated sample (the actual cost depends on the number and type of target constituents). Recent advances in applied technology have facilitated the use of field gas chromatographs (GCs) to automatically obtain analytical results for many organics (i.e., offsite laboratory analyses may not be necessary for some air monitoring programs). The cost for this equipment typically range from $20,000 to over $50,000 and one GC can generally service multiple sampling stations.

An example sampling schedule (e.g., for flat terrain sites with minimal variability of dispersion and source conditions) for meeting this objective is given below:

- Meteorological monitoring - 90 days continuous monitoring.

- Initial air monitoring (Alternative 1) -90 days:
  - Analysis of 24-hour time integrated samples for target constituents every day during the 90-day period (total of 90 samples)

- Additional monitoring - as necessary to supplement initial air monitoring results in order to adequately characterize the release.

The 90-day monitoring program will facilitate collecting samples over a wide range of emission and dispersion conditions. The 90-day period should be selected, as previously discussed, to coincide with the expected season of highest ambient concentrations. Meteorological monitoring should be continuous and concurrent with this 90-day period to adequately characterize dispersion conditions at the site and to provide meteorological data to support interpretation of the air-quality monitoring data.

The collection of a time-integrated sample based on continuous monitoring for several days can result in technical difficulties (e.g., poor collection efficiencies for volatile constituents or large sample volumes). The application of five-day composite samples at each station, or intermittent sampling during the five days, results in continuous monitoring coverage during the 90-day period and facilitates the characterization of long-term exposure levels.

Although there are some limitations associated with composite/intermittent sampling (e.g., the potential for sample degradation), the 24-hour samples collected every sixth day will provide a second data set for characterizing ambient concentrations. Although the results of the two data sets should not be directly combined (because of the different sampling periods) they provide a comprehensive technical basis by which to evaluate long-term exposure conditions.

12.6.4.4 Subsequent Monitoring

Subsequent monitoring may be necessary if initial monitoring data were not sufficient to estimate "reasonable worst case" long-term concentrations (e.g., data recovery was not sufficient or additional monitoring stations are needed).

The same schedule specified for the initial monitoring phase is also applicable to subsequent monitoring. However, when evaluating the results of subsequent monitoring and comparing them to previously collected data, potential differences in emission/dispersion conditions and other data representativeness factors should be accounted for.

12.6.5 Monitoring Approach

The RFI air release characterization strategy may involve source emission monitoring and/or air monitoring. The strategy which defines the process for selection and application of these alternative monitoring approaches has been discussed previously. A summary of applicable air monitoring strategies related to source type is presented in Table 12-10.

TABLE 12-10
APPLICABLE AIR RELEASE SAMPLING STRATEGIES BY SOURCE TYPE

Unit Type/Expected Emission	Air Release Sampling Strategy		
		Emissions Monitoring	
	Air Monitoring	Vent/Stack Sampling	Isolation Flux Chambers
AREA SOURCES WITH LIQUID SURFACES			
Surface Impoundments			
Vapor Phase	X		X
Particulates	X		
Open Roof Storage/Treatment Tanks			
Vapor Phase	X	X	X
AREA SOURCES WITH SOLID SURFACES			
Waste Piles			
Vapor Phase	X		X
Particulates	X		
Landfill Surface			
Vapor Phase	X		X
Particulates	X		
Land Treatment			
Vapor Phase	X		X
Particulates	X		
POINT SOURCES			
Vents from container Handling Units			
Vapor Phase	X	X	
Landfill Vents			
Vapor Phase	X	X	X
Storage/Treatment Tank Vents			
Vapor Phase	X	X	
Incinerators			
Vapor Phase	X	X	
Particulates	X	X	

12.6.5.1 Source Emissions Monitoring

Monitoring at the source to measure a rate of emission for the constituents of concern may, in many cases, offer a practical approach to characterizing air emissions. Using this technique, the emission rate is then input into a mathematical dispersion model for estimation of downwind concentrations. Monitoring interferences from sources close to the unit are eliminated because the source is isolated from the ambient atmosphere for monitoring purposes. Source monitoring techniques are also advantageous because they do not require the level of sensitivity required by air monitors. Concentrations of airborne constituents at the source are generally higher than at downwind locations due to the lack of dispersion of the constituent over a wide area. The concentrations expected in the air (generally part-per-billion levels) may be at or near the limit of detectability of the methods used. Methods for source emissions monitoring for various constituent classes are discussed in Section 12.8.

Area sources (such as landfills, land treatment units, and surface impoundments) can be monitored using the isolation flux chamber approach. This method involves isolating a small area of contamination under a flux chamber, and passing a known amount of a zero hydrocarbon carrier gas through the chamber, thereby picking up any organic emissions in the effluent gas stream from the flux chamber. Samples of this effluent stream are collected in inert sampling containers, usually stainless steel canisters under vacuum, and removed to the laboratory for subsequent analysis. The analytical results of the identified analytes can be converted through a series of calculations to direct emission rates from the source. These emission rates can be used to evaluate downwind concentrations by application of dispersion models. Multiple emission tests should be conducted to account for temporal and spatial variability of source conditions. More information on use of the isolation flux chamber and test design is provided in the following references:

U.S. EPA. 1986. Measurement of Gaseous Emission Rates from Land Surfaces Using an Emission Isolation Flux Chamber: User's Guide. EPA/600/8-86/008. NTIS PB 86-223161. Washington, D.C. 20460.

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U.S. EPA. December 1988 Draft. Procedures for Conducting Air Pathway Analyses for Superfund Applications. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

Some area source units may not be amenable to the source sampling approach, however. A unit in which the source cannot be isolated and viable measurements taken of the parameters of concern is one example. This includes active areas of landfills and land-treatment areas, as well as aerated surface impoundments. Also, area sources in which particulate emissions are of concern cannot be measured using an isolation flux chamber due to technical limitations in the technique. For these applications, only an upwind/downwind monitoring approach should be used.

12.6.5.2 Air Monitoring

Use of an upwind/downwind network of monitors or sample collection devices is the primary air monitoring approach recommended to determine release and background concentrations of the constituents of concern. Upwind/downwind air monitoring networks provide concentrations of the constituents of concern at the point of monitoring, whether at the unit boundary, facility property boundary, or at a receptor point. The upwind/downwind approach involves the placement of monitors or sample collection devices at various points around the unit of concern. Each air sample collected is classified as upwind or downwind based on the wind conditions for the sampling period. Downwind concentrations are compared to those measured at upwind points to determine the relative contribution of the unit to air concentrations of toxic compounds. This is generally accomplished by subtracting the upwind concentration (which represents background conditions) from the concurrent downwind concentrations. Applicable field methods for air monitoring are discussed in Section 12.8 as well as in Procedures for Conducting Air Pathway Analyses for Superfund Applications (U.S. EPA, December 1988). Downwind air concentrations at the facility can be extrapolated to other locations by using dispersion modeling results. This is accomplished by obtaining initial modeling results based on meteorological conditions for the monitoring period and an arbitrary emission rate. These initial dispersion modeling results along with monitoring results at the site perimeter are used to back calculate an emission rate such that modeling results can be adjusted to be equivalent to monitoring results at

the onsite monitoring station. This estimated emission rate is then used as dispersion modeling input to predict offsite concentrations.

12.6.6 Monitoring Locations

As with other factors associated with air monitoring, siting of the monitors should reflect the primary objective of characterizing concentrations at the facility property boundary. This section discusses monitoring locations for both upwind/downwind approaches and source monitoring techniques.

12.6.6.1 Upwind/Downwind Monitoring Locations

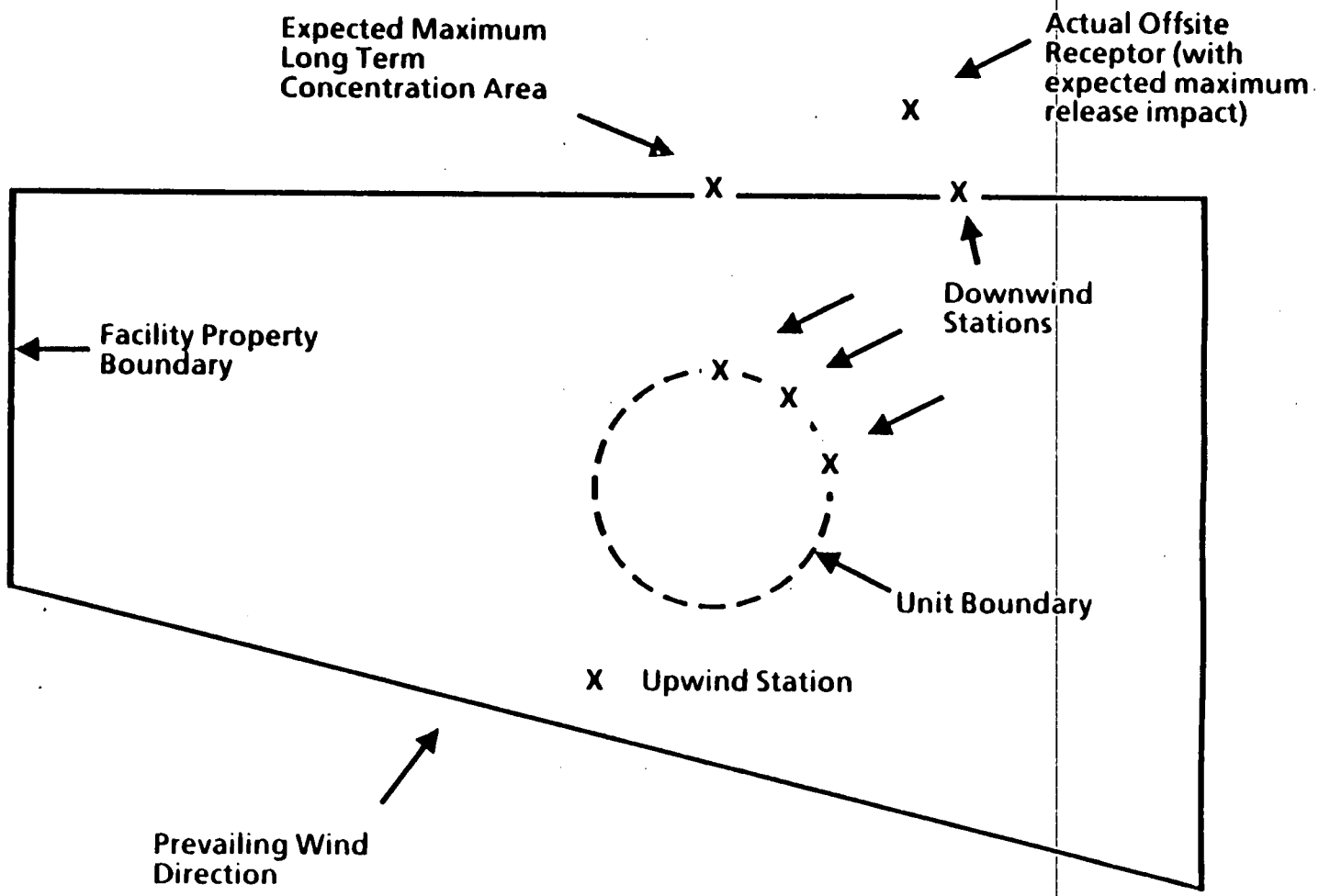
The air monitoring network design should provide adequate coverage to characterize both upwind (background) and downwind concentrations. Therefore, four air monitoring zones are generally necessary for initial monitoring. Multiple monitoring stations per zone will frequently be required to adequately characterize the release. An upwind zone is used to define background concentration levels. Downwind zones at the unit boundary, at the facility property boundary and beyond the facility property boundary, if appropriate, are used to define potential offsite exposure.

The location of air monitoring stations should be based on local wind patterns. Air monitoring stations should be placed at strategic locations, as illustrated in the following example (see Figure 12-6).

- Upwind (based on the expected prevailing wind flow during the 90-day monitoring period) of the unit and near the facility property boundary to characterize background air concentration levels. There should be no air emission source between the upwind monitoring station and the unit boundary.

- Downwind (based on the expected prevailing wind flow during the 90-day monitoring period) at the unit boundary plus stations at adjacent sectors also at the unit boundary (the separation distance of air monitoring stations at the unit boundary should be 30° or 50 feet, whichever is greater).

FIGURE 12-6. EXAMPLE AIR MONITORING NETWORK



- Downwind (based on the expected prevailing wind flow during the 90-day monitoring period) at the facility property boundary (this station may not be required if the site perimeter is within 100 meters of the unit boundary).

- Downwind (at the area expected to have the highest average concentration levels during the 90-day monitoring period) at the facility property boundary, if appropriate.

- Downwind at actual offsite receptor locations (if appropriate).

- Additional locations at complex terrain and coastal sites associated with pronounced secondary air flow paths (e.g., downwind of the unit near the facility property boundary for both primary daytime and nighttime flow paths).

The above locations should be selected prior to initial monitoring based on the onsite meteorological survey and on evaluation of available representative offsite meteorological data. This analysis should provide an estimate of expected wind conditions during the 90-day initial monitoring period. If sufficient representative data are available, dispersion modeling can be used to identify the area of maximum long term concentration levels at the facility property boundary and, if appropriate, at actual offsite receptors. If not, the facility property boundary sector nearest to the unit of concern should be selected for initial monitoring.

The network design defined above will provide an adequate basis to define long-term concentrations based on continuous monitoring during the 90-day initial monitoring period. The monitoring stations at the unit boundary should increase the potential for release detection. The facility property boundary air monitoring stations should provide data (with the aid of dispersion modeling, if appropriate) to perform health and environmental assessment, and if appropriate, characterize offsite concentrations.

Air monitoring at offsite receptors (if deemed to be appropriate) may be impractical in many cases, because analytical detection limits may not be low

enought at offsite receptor locations to measure the release. Also, a 90-day offsite monitoring program can be problematic. Factors such as vandalism, erroneous readings due to public tampering with the equipment, public relations problems in setting up the equipment, and legal access problems may preclude the use of offsite air monitoring stations. For these cases, dispersion models may be used to extrapolate monitoring data collected at the facility to actual offsite receptor locations. This is accomplished by obtaining initial modeling results based on meteorological conditions for the monitoring period and an arbitrary emission rate. These initial dispersion modeling results along with monitoring results at the site perimeter are used to back calculate an emission rate such that modeling results can be adjusted to be equivalent to monitoring results at the onsite monitoring station. This estimated emission rate is then used as dispersion modeling input to predict offsite concentrations for the same downwind sector and exposure period as for this monitoring period.

If additional monitoring is required, a similar network design to that illustrated in Figure 12-6 will generally be appropriate. Evaluation of the meteorological monitoring data collected during the initial phase should provide an improved basis to identify local prevailing and diurnal wind flow paths. Also, the site meteorological data will provide dispersion modeling input. These modeling results should provide dilution patterns that can be used to identify areas with expected relatively high concentration levels. However, these results should account for seasonal meteorological differences between initial and additional monitoring periods.

Wind-directionally controlled air monitoring stations can also be used at sites with highly variable wind directions. These wind-directionally controlled stations should be collocated with the fixed monitoring stations. This approach facilitates determination of the unit source contribution to total constituent levels in the local area. These automated stations will only sample for a user-defined range of wind directions (e.g., downwind stations would only sample if winds were blowing from the source towards the station). Interpretation of results from wind-directionally controlled air monitoring stations should account for the lower sampling volumes (and therefore, the possibility that not enough sample would be collected for analysis) generally associated with this approach.

The inlet exposure height of the air monitors should be 2 to 15 meters to be representative of potential inhalation exposure but not unduly biased by road dust and natural wind erosion phenomena. Further guidance on air monitoring network design and station exposure criteria (e.g., sampling height and proximity to structures and air emission sources) is provided in the following reference:

U.S. EPA. September 1984. Network Design and Site Exposure Criteria for Selected Non-criteria Air Pollutants. EPA-450/4-84-022. Office of Air Quality Planning and Standards. Research Triangle Park, N.C.

The above referenced document recommends the use of dispersion models to identify potential relatively high concentration areas as a basis for network design. This topic is also discussed in the following document:

U.S. EPA. July 1986. Guidelines on Air Quality Models (Revised). EPA-450/2-78-027R. NTIS PB 86-245248. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

Uniformity among the sampling sites should be achieved to the greatest degree possible. Descriptions should be prepared for all sampling sites. The description should include the type of ground surface, and the direction, distance, and approximate height with respect to the source of the release. Location should also be described on a facility map.

12.6.6.2 Stack/Vent Emission Monitoring

Point source measurements should be taken in the vent. Both the VOST and Modified Method 5 methodologies describe the exact placement in the stack for the sampler inlet. (See Section 12.8.3). If warranted, an upwind/downwind monitoring network can be used to supplement the release rate data.

12.6.6.3 Isolation Flux Chambers

Monitor placement using flux chambers (discussed earlier) is similar to conducting a characterization of any area source. Section 3 of this guidance discusses establishment of a grid network for sampling. Such a grid should be

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established for an area source, with sampling points established within the grids, as appropriate. It is suggested that a minimum of six points be chosen for each monitoring effort. Once these areas are sampled, the results can be temporally and spatially averaged to provide an overall compound specific emission rate for the plot. Additional guidance on monitoring locations for isolation flux chambers is presented in Section 3.6 and in the following references:

U.S. EPA. 1986. Measurement of Gaseous Emission Rates from Land Surfaces Using an Emission Isolation Flux Chamber: User's Guide. EPA/600/8-86/008. NTIS PB86-223161. Environmental Monitoring Systems Laboratory. Las Vegas, NV 89114.

U.S. EPA. December 1988 Draft. Procedures for Conducting Air Pathway Analyses for Superfund Applications. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

12.7 Data Presentation

As discussed in Section 5, progress reports will be required by the regulatory agency at periodic intervals during the investigation. The following data presentation formats are suggested for the various phases of the air investigation in order to adequately characterize concentrations at actual offsite receptors.

12.7.1 Waste and Unit Characterization

Waste and unit characteristics should be presented as:

- Tables of waste constituents and concentrations;
- Tables of relevant physical/chemical properties for potential air emission constituents;
- Tables and narratives describing unit dimensions and special operating conditions and operating schedules concurrent with the air monitoring program;

- Narrative description of unit operations; and

- Identification of "reasonable worst case" emission conditions that occurred during the monitoring period.

12.7.2 Environmental Setting Characterization

Environmental characteristics should be presented as follows:

- Climate (historical summaries from available onsite and offsite sources):

  - Annual and monthly or seasonal wind roses;

  - Annual and monthly or seasonal tabular summaries of mean wind speeds and atmospheric stability distributions; and

  - Annual and monthly or seasonal tabular summaries of temperature and precipitation.

- Meteorological survey results:

  - Hourly listing of all meteorological parameters for the entire monitoring period;

  - Daytime wind rose (at coastal or complex terrain sites);

  - Nighttime wind rose (at coastal or complex terrain sites);

  - Summary wind rose for all hours;

  - Summary of dispersion conditions for the monitoring period (joint frequency distributions of wind direction versus wind speed category and stability class frequencies); and

  - Tabular summaries of means and extremes for temperature and other meteorological parameters.

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- Definition of soil conditions (if appropriate):

  - Narrative of soil characteristics (e.g., temperature, porosity and organic matter content); and

  - Characterization of soil contamination conditions (e.g., in land treatment units, etc.).

- Definition of site-specific terrain and nearby receptors:

  - Topographic map of the site area with identification of the units, meteorological and air monitoring stations, and facility property boundary;

  - Topographic map of 10-kilometer radius from site (U.S. Geological Survey 7.5 minute quadrangle sheets are acceptable); and

  - Maps which indicate location of nearest residence for each of sixteen 22.5 degree sectors which correspond to major compass points (e.g., north, north-northwest, etc.), nearest population centers and sensitive receptors (e.g., schools, hospitals and nursing homes).

- Maps showing the topography of the area, location of the unit(s) of concern, and the location of meteorological monitoring equipment.

- A narrative description of the meteorological conditions during the air sampling periods, including qualitative descriptions of weather events and precipitation which are needed for data interpretation.

12.7.3 Characterization of the Release

Characteristics of the release should be presented as follows:

- Screening sampling:

- Identification of sampling and analytical methodology;

- Map which identifies sampling locations;

- Listing of measured concentrations indicating collection time period and locations;

- Prioritization of units as air release sources which warrant monitoring based on screening results;

- Discussion of QA/QC results; and

- Listing and discussion of meteorological data during the sampling period.

- Initial and additional monitoring results:

  - Identification of monitoring constituents;

  - Discussion of sampling and analytical methodology as well as equipment and specifications;

  - Identification of monitoring zones as defined in Section 12.6.6.1;

  - Map which identifies monitoring locations relative to units;

  - Discussion of QA/QC results;

  - Listing of concentrations measured by station and monitoring period indicating concentrations of all constituents for which monitoring was conducted. Listings should indicate detection limits if a constituent is not detected;

  - Summary tables of concentration measured indicating maximum and mean concentration values for each monitoring station;

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- Discussion of meteorological station locations selection, sensor height, local terrain, nearby obstructions and equipment specifications;

- Listing of all meteorological parameters concurrent with the air sampling periods;

- Daytime wind rose (only for coastal or complex terrain areas);

- Nighttime wind rose (only for coastal or complex terrain areas);

- Summary wind rose based on all wind direction observations for the sampling period;

- Summary of dispersion conditions for the sampling period (joint frequency distributions of wind direction versus wind speed category and stability class frequencies based on guidance presented in Guidelines on Air Quality Models (Revised), (U.S. EPA, July 1986));

- Tabular summaries of means and extremes for temperature and other meteorological parameters;

- A narrative discussion of sampling results, indicating problems encountered, relationship of the sampling activity to unit operating conditions and meteorological conditions, sampling periods and times, background levels and identification of other air emission sources and interferences which may complicate data interpretation;

- Presentation and discussion of models used (if any), modeling input data and modeling output data (e.g., dilution or dispersion patterns based on modeling results); and

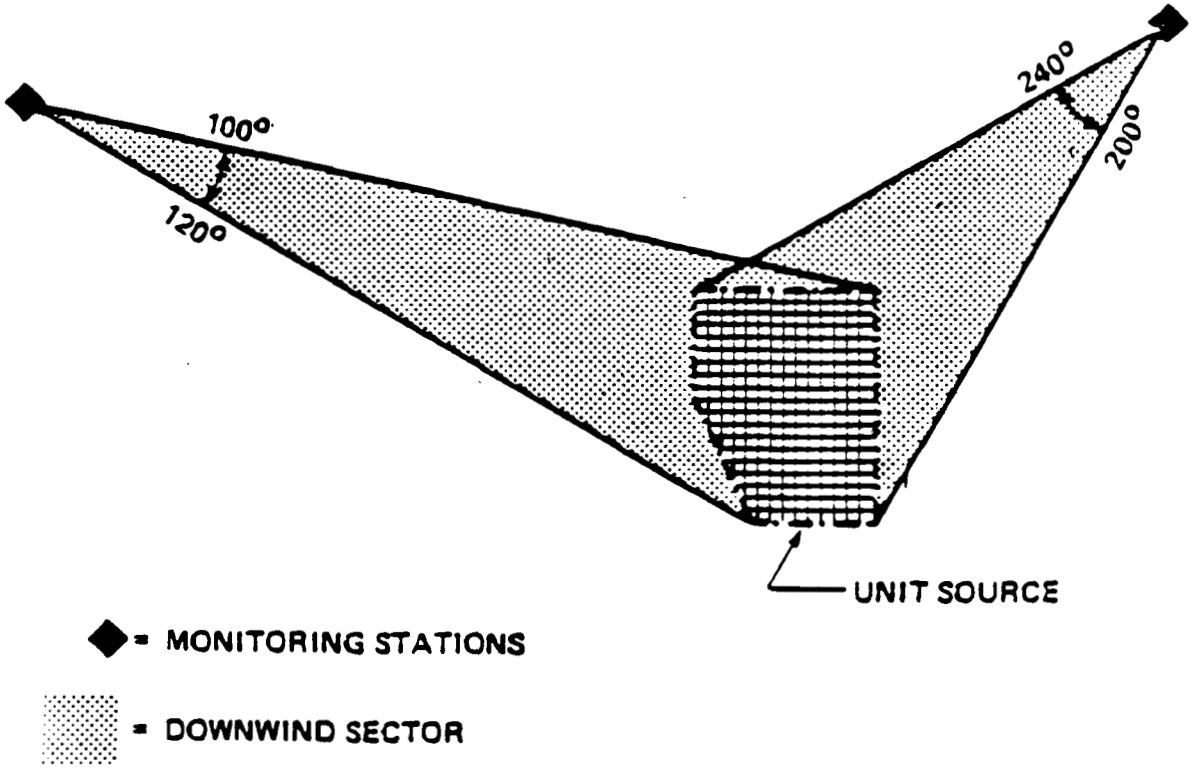
- Concentrations based on monitoring and/or modeling for actual offsite receptor locations.

Interpretation of air monitoring results should also account for additional factors such as complex terrain, variable winds, multiple contaminant sources and intermittent or irregular releases. The key to data interpretation for these cases is to evaluate monitoring results as a function of wind direction.

Terrain factors can alter wind flow trajectories especially during stable nighttime conditions. Therefore, straightline wind trajectories may not occur during these conditions if there is intervening terrain between the source and the air monitoring station. For these cases wind flows will be directed around large obstacles (such as hills) or channeled (for flows within valleys). Therefore, it is necessary to determine the representativeness of the data from the meteorological stations as a function of wind direction, wind speed and stability conditions. Based on this assessment, and results from the meteorological survey, upwind and downwind sectors (i.e., a range of wind direction as measured at the meteorological station) should be defined for each air monitoring station to aid in data interpretation. Figure 12-7 illustrates an example which classifies a range of wind directions during which the air monitoring stations will be downwind of an air emission source. Therefore, concentrations measured during upwind conditions can be used to characterize background conditions and concentrations measured during downwind conditions can be used to evaluate the air-quality impact of the release.

Complex terrain sites and coastal sites frequently have very pronounced diurnal wind patterns. Therefore, as previously discussed, the air monitoring network at these sites may involve coverage for multiple wind direction sectors and use of wind-directionally controlled air samplers. This monitoring approach is also appropriate for sites with highly variable wind conditions. Comparing results from two collocated air monitoring stations (i.e., one station which samples continuously and a second station at the same location which is wind-directionally controlled on an automated basis), facilitates determination of source contributions to ambient air concentrations.

FIGURE 12-7
EXAMPLE OF DOWNWIND EXPOSURES AT AIR MONITORING STATIONS



Comparison of results from collocated (continuous versus wind-directionally controlled) air monitoring stations can also be used to assist in data interpretation at sites with multiple air emission sources or with intermittent/irregular releases. For some situations, the consistent appearance of certain air emission constituents can be used to "fingerprint" the source. Therefore, the air monitoring results can be classified based on these "fingerprint" patterns. These results can then be summarized as two separate data sets to assess background versus source contributions to ambient concentrations.

The use of collocated (continuous and wind-directionally controlled) air monitoring stations is a preferred approach to data interpretation for complex terrain, variable wind, multiple source and intermittent release sites. An alternative data interpretation approach involves reviewing the hourly meteorological data for each air sampling period. Based on this review, the results from each sampling period (generally a 24-hour period) for each station are classified in terms of downwind frequency. The downwind frequency is defined as the number of hours winds were blowing from the source towards the air monitoring station divided by the total number of hours in the sampling period. These data can then be processed (by plotting scattergrams) to determine the relationship of downwind frequency to measured concentrations.

Data interpretation should also take into account the potential for deposition, degradation and transformation of the monitoring constituents. These mechanisms can affect ambient concentrations as well as air sample chemistry (during storage). Therefore, standard technical references on chemical properties, as well as the monitoring guidance previously cited, should be consulted to determine the importance of degradation and transformation for the monitoring constituents of concern.

12.8 Field Methods

This section describes field methods which can be used during initial or subsequent monitoring phases. Methods are classified according to source type and area. Guidance on meteorological monitoring methods is also provided in this section.

12.8.1 Meteorological Monitoring

Meteorological monitoring generally should employ a 10-meter tower equipped with wind direction, wind speed, temperature and atmospheric stability instrumentation. Wind direction and wind speed monitors should exhibit a starting threshold of less than 0.5 meters per second (m/s). Wind speed monitors should be accurate above the starting threshold to within 0.25 m/s at speeds less than or equal to 5 m/s. At higher speeds the error should not exceed 5 percent of the wind speed. Wind direction monitor errors should not exceed 5 degrees. Errors in temperature should not exceed 0.5°C during normal operating conditions.

The meteorological station should be installed at a location which is representative of overall site terrain and wind conditions. Multiple meteorological station locations may be required at coastal and complex terrain sites.

Additional guidance on equipment performance specifications, station location, sensor exposure criteria, and field methods for meteorological monitoring are provided in the following references:

U.S. EPA. February 1983. Quality Assurance Handbook for Air Pollution Measurement Systems: Volume IV, Meteorological Measurement. EPA-600-4-82-060. Office of Research and Development. Research Triangle Park, NC 27711.

U.S. EPA. November 1980. Ambient Monitoring Guidelines for Prevention of Significant Deterioration (PSD). EPA-450/4-80-012. NTIS PB 81-153231. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

U.S. EPA. July 1986. Guidelines on Air Quality Models (Revised). EP-450/2-78-027R. NTIS PB 86-245248. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

12.8.2 Air Monitoring

Selection of methods for monitoring air contaminants should consider a number of factors, including the compounds to be detected, the purpose of the

method (e.g., screening or quantification), the detection limits, and sampling rates and duration required for the investigation.

Organic and inorganic constituents require different analytical methods. Within these two groups, different methods may also be required depending on the constituent and its physical/chemical properties. Another condition that affects the choice of monitoring technique is whether the compound is primarily in the gaseous phase or is found adsorbed to solid particles or aerosols.

Screening for the presence of air constituents involves techniques and equipment that are rapid, portable, and can provide "real-time" monitoring data. Air contamination screening will generally be used to confirm the presence of a release, or to establish the extent of contamination during the screening phase of the investigation. Quantification of individual components is not as important during screening as during initial and additional air monitoring, however the technique must have sufficient specificity to differentiate hazardous constituents of concern from potential interferences, even when the latter are present in higher concentrations. Detection limits for screening devices are often higher than for quantitative methods.

Laboratory analytical techniques must provide positive identification of the components, and accurate and precise measurement of concentrations. This generally means that preconcentration and/or storage of air samples will be required. Therefore, methods chosen for quantification usually involve a longer analytical time-period, more sophisticated equipment, and more rigorous quality assurance procedures.

The following list of references provides guidance on air monitoring methodologies:

U.S. EPA. June 1983. Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air. EPA-600/4-83-027. NTIS PB 83-239020. Office of Research and Development. Research Triangle Park, NC 27711.

U.S. EPA. April 1984. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. EPA-600/4-84-041. Office of Research and Development. Research Triangle Park, NC 27711.

NIOSH. February 1984. NIOSH Manual of Analytical Methods. NTIS PB 85-179018. National Institute for Occupational Safety and Health. Cincinnati, OH.

U.S. EPA. September 1983. Characterizaiton of Hazardous Waste Sites - A Methods Manual: Volume II, Available Sampling Methods. EPA-600/4-83-040. NTIS PB 84-126929. Office of Solid Waste. Washington, D.C. 20460.

U.S. EPA. September 1983. Characterization of Hazardous Waste Sites - A Methods Manual: Volume III, Available Laboratory Analytical Methods. EPA-600/4-83-040. NTIS PB 84-126929. Office of Solid Waste. Washington, D.C. 20460.

U.S. EPA. 1986. Test Methods for Evaluating Solid Waste. 3rd Edition. EPA SW-846. GPO No 955-001-00000-1. Office of Solid Waste. Washington, D.C. 20460.

ASTM. 1982. Toxic Materials in the Atmosphere. ASTM, STP 786. Philadelphia, PA.

ASTM. 1980. Sampling and Analysis of Toxic Organics in the Atmosphere. ASTM, STP 721. Philadelphia, PA.

ASTM. 1974. Instrumentation for Monitoring Air Quality. ASTM, STP 555. Philadelphia, PA.

APHA. 1977. Methods of Air Sampling and Analysis. American Public Health Association. Cincinnati, OH.

ACGIH. 1983. Air Sampling Instruments for Evaluation of Atmospheric Contaminants. American Conference of Governmental Industrial Hygienists. Washington, D.C.

U.S. EPA. December 1988 Draft. Procedures for Conducting Air Pathway Analyses for Superfund Applications. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711.

12.8.2.1 Screening Methods

Screening techniques for vapor-phase constituents fall into two main categories. (1) organic and non-organic compound-specific indicators, and (2) general organic detectors. Table 12-11 presents a summary of commercially available screening methods for these compounds.

Indicator tubes and other colorimetric methods--Indicator tubes, also known as gas detector or Draeger tubes, are small glass tubes filled with a reagent-coated material which changes color when exposed to a particular chemical. Air is pulled through the tube with a low-volume pump. Tubes are available for 40 organic gases, and for 8 hour or 15 minute exposure periods. Indicator tubes were designed for use in occupational settings, where high levels of relatively pure gases are likely to occur. Therefore, they have only limited usefulness for ambient air sampling, where part-per-billion levels are often of concern. However, because they are covenient to use and available for a wide range of compounds, detector tubes may be useful in some screening/sampling situations.

Other colorimetric methods, such as continuous flow and tape monitor techniques, were developed to provide real-time monitoring capability with indicator methods. The disadvantages of these systems are similar to those of indicator tubes.

Instrument detection screening methods--More commonly used for volatile organic surveys, portable instrument detection methods include flame ionization detectors (FID), photoionization detectors (PID), electron capture detectors (ECD), and infrared detectors (ID). Also in use are detectors that respond to specific chemical classes such as sulfur- and nitrogen-containing organics. These instruments are used to indicate levels of total organic vapors and for identification of " hot zones" downwind of the release source(s). They can be used as real-time non-specific monitors or, by adding a gas chromatograph, can provide concentration estimates and tentative identification of pollutants.

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TABLE 12-11
TYPICAL COMMERCIALLY AVAILABLE SCREENING TECHNIQUES FOR ORGANICS IN AIR (FROM RIGGIN, 1983)

Technique	Manufacturers	Compounds Detected	Approximate Detection Limit	Comments
Gas Detection Tubes	Draeger Matheson Kitagawa	Various organics and inorganics	0.1 to 1 ppmv	Sensitivity and selectivity highly dependent on component of interest.
Continuous Flow Colorimeter	CEA Instruments, Inc.	Acrylonitrile, formaldehyde, phosgene, and various organics	0.05 to 0.5 ppmv	Sensitivity and selectivity similar to detector tubes.
Colorimetric Tape Monitor	KHDA Scientific	Toluene, diisocyanate, dinitro toluene, phosgene, and various inorganics	0.05-0.5 ppmv	Same as above.
Infrared Analysis	Foxboro/Wilkes	Most organics	1-10 ppmv	Some inorganic gases (H_20, CO) will be detected and therefore are potential interferences.
FID (Total Hydrocarbon Analyzer)	Beckman HSA, Inc. AID, Inc.	Most organics	0.5 ppmv	Responds uniformly to most organic compounds on a carbon basis.
GC/FID (portable)	Foxboro/Century AID, Inc.	Same as above except that polar compounds may not elute from the column.	0.5 ppmv	Qualitative as well as quantitative information obtained.
PID and GC/PID (portable)	HNU, Inc. AID, Inc. Photovac, Inc.	Most organic compounds can be detected with the exception of methane	0.1 to 100 ppbv	Selectivity can be adjusted by selection of lamp energy. Aromatics most readily detected.
GC/ECD (portable)	AID, Inc.	Halogenated and nitro-substituted compounds	0.1 to 100 ppbv	Response varies widely from compound to compound.
GC/FPD (portable)	AID, Inc.	Sulfur or phosphorus-containing compounds	10-100 ppbv	Both inorganic and organic sulfur or phosphorus compounds will be detected.
Chemiluminescent Nitrogen Detector	Antek, Inc.	Nitrogen-containing compounds	0.1 ppmv (as N)	Inorganic nitrogen compounds will interfere.

Of the available detectors, those that are the most applicable to an RFI are the FID and PID. Table 12-12 summarizes four instruments (two FID and two PID versions) which are adequate for the purposes of the screening phase.

Flame Ionization Detectors--The Century OVA 100 series and AID Model 550 utilize a FID to determine the presence of vapor phase organics. The detector responds to the total of all organics present in the air at any given moment. Flame ionization detectors will respond to most organics, but are most sensitive to hydrocarbons (i.e., those chemicals which contain only carbon and hydrogen molecules such as benzene and propane). FIDs are somewhat less sensitive to compounds containing chlorine, nitrogen, oxygen, and sulfur molecules. The response is calibrated against a reference gas, usually methane. FID response is often termed "total hydrocarbons"; however, this is misleading because particulate hydrocarbons are not detected. FID detection without gas chromatography is not useful for quantification of individual compounds, but provides a useful tool for general assessment purposes. Detection limits using a FID detector alone are about 1 ppm. Addition of a gas chromatograph (GC) lowers the detection limit to ppb levels, but increases the analysis time significantly.

Photoionization Detectors--Portable photoionization detectors such as the HNU Model PI-101 and the Photovac 10A10 operate by applying UV ionizing radiation to the contaminant molecules. Some selectivity over the types of organic compounds detected can be obtained by varying energy of the ionizing beam. In the screening mode this feature can be used to distinguish between aliphatic and aromatic hydrocarbons and to exclude background gases from the instrument's response. The HNU and Photovac can be used either in the survey mode (PID only), or with GC. Sensitivity with PID alone is about 1 ppm, but can go down to as low as 0.1 ppb when a GC is used.

PI and FI detectors used in the GC mode can be used for semiquantitative analysis of compounds in ambient air. However, in areas where numerous contaminants are present, identification of peaks in a complex matrix may be tentative at best.

TABLE 12-12

SUMMARY OF SELECTED ONSITE ORGANIC SCREENING METHODOLOGIES

Instrument or detector	Measurable parameters	Low range of detection	Comments
Century Series 100 or AID Model 550 (survey mode)	Volatile organic species	Low ppm	Uses Flame Ionization Detector (FID)
HNU Model PI-101	Volatile organic species	Low ppm	Photo-ionization (PI) detector-provides especially good sensitivity to low molecular weight aromatic compounds (i.e., benzene, toluene)
Century Systems OVA-128 (GC mode)	Volatile organic species	Low ppm	Uses GC column for possible specific compound identification
Photo Vac 10A10	Volatile organic species	Low ppm	Uses PI detector. Especially sensitive to aromatic species. May be used for compound identification if interferences are not present

Another method which can be used as a survey technique is mobile mass spectrometry. Ambient air is drawn through a probe directly into the instrument, which is usually mounted in a van. Particularly in the MS/MS configuration this is a powerful technique which can provide positive identification and semiquantitative measurement of an extrememly wide range of organic and inorganic gaseous contaminants.

12.8.2.2 Quantitative Methods

Laboratory analysis of hazardous constituents in air includes the following standard steps:

- Preconcentration of organics (as necessary to achieve detection limit goals);
- Transfer to a gas chromatograph or HPLC (High Pressure Liquid Chromatography); and
- Quantification and/or identification with a detector.

Broad-spectrum methods applicable to most common air contaminants are discussed below.

12.8.2.2.1 Monitoring Organic Compounds in Air

Due to the large number of organic compounds that may be present in air, and their wide range in chemical and physical properties, no single monitoring technique is applicable to all organic air contaminants. Numerous techniques have been developed, and continue to be developed, to monitor for specific compound classes, individual chemicals, or to address a wide range of hazardous contaminants. This last approach may be the most efficient approach to monitoring at units where a wide range of chemicals are likely to be present. Therefore, methods that apply to a broad range of compounds are recommended. In cases where specific compounds of concern are not adequately measured by broad-spectrum methods, compound-specific techniques are described or referenced.

12.8.2.2.1.1 Vapor-Phase Organics

The majority of hazardous constituents of concern can be classified as gaseous or (vapor-phase) organics. These constituents include most petroleum-related hydrocarbons, organic solvents, and many pesticides, and other semivolatile organic compounds. Methods to monitor these compounds generally include on-site analysis (making use of onsite concentration techniques, where necessary), or require storage in a tightly sealed non-reactive container.

Techniques for volatile and semivolatile organics measurement include:

- Adsorption of the sample on a solid sorbent with subsequent desorption (thermal or chemical), followed by gas chromatographic analysis using a variety of detectors.

- Collection of whole air (grab) samples in an evacuated flask or in Tedlar or Teflon bags, with direct injection of the sample into a GC using high sensitivity and/or constituent-specific detectors. This analysis may or may not be preceded by a preconcentration step.

- Cryogenic trapping of samples in the field with subsequent instrumental analysis.

- Bubbling ambient air through a liquid-filled impinger, containing a chemical that will absorb or react with specific compounds to form more stable products for GC analysis.

- Direct introduction of the air into a MS/MS or other detector.

Tables 12-13 (A and B), 12-14, and 12-15 summarize sampling and analytical techniques that are applicable to a wide range of vapor phase organics, have been widely tested and validated in the literature, and make use of equipment that is readily available. A discussion of general types of techniques is given below.

TABLE 12-13A. SUMMARY OF CANDIDATE METHODOLOGIES FOR QUANTIFICATION OF VAPOR PHASE ORGANICS

Collection Technique	Analytical Technique	Applicability (See Table 12-15B)	Positive Aspects	Negative Aspects
I. Sorption onto Tenax-GC or carbon molecular sieve packed cartridges using low-volume pump	Thermal Desorption into GC or GC/MS	I	• adequate QA/QC data base • widely used on investigations around uncontrolled waste sites • wide range of applicability • μ/m^3 detection limits • practical for field use	• possibility of contamination • artifact formation problems • rigorous cleanup needed • no possibility of multiple analysis • low breakthrough volumes for some compounds
II. Sorption onto charcoal packed cartridges using low-volume pump	Resorption with solvent-analysis by GC or GC/MS	II	• large data base for various compounds • wide use in industrial applications • practical for field use	• problems with irreversible adsorption of some compounds • high (mg/m^3) detection limits • artifact formation problems • high humidity reduces retention efficiency
III. Sorption onto polyurethane foam (PUF) using low-volume or high-volume pump	Solvent extraction of PUF; analysis by GC/MS	I, II, III	• wide range of applicability • easy to preclean and extract • very low blanks • excellent collection and retention efficiencies • reusable up to 10 times	• possibility of contamination • losses of more volatile compounds may occur during storage
IV. Sorption on passive dosimeters using Tenax or charcoal as adsorbing medium	Analysis by chemical or thermal desorption following by GC or GC/MS	I or II	• samplers are small, portable, require no pumps • makes use of analytical procedures of known precision and accuracy for a broad range of compounds • pg/m^3 detection limits	• problems associated with sampling using sorbents • uncertainty in volume of air sampled makes concentration calculations difficult • requires minimum external air flow rate

TABLE 12-13A (Continued)

Collection Technique	Analytical Technique	Applicability (see Table 12-15B)	Positive Aspects	Negative Aspects
V. Cryogenic trapping of analytes in the field	Desorption into GC	II, III	• applicable to a wide range of compounds • artifact formation minimized • low blanks	• requires field use of liquid nitrogen or oxygen • sample is totally used in one analysis - no reanalysis possible • samplers easily clogged with water vapor • no large data base on precision or recoveries
VI. Whole air sample taken in glass or stainless steel bottles	Cryogenic trapping or direct injection into GC or GC/MS (onsite or laboratory analysis)	II, III	• useful for grab sampling • large data base • excellent long-term storage • wide applicability • allows multiple analyses	• difficult to obtain integrated samples • low sensitivity if preconcentration is not used
VII. Whole air sample taken in Tedlar[K] Bag	Cryogenic trapping or direct injection into GC or GC/MS (onsite or laboratory)	II, III	• grab or integrated sampling • wide applicability • allows multiple analyses	• long-term stability uncertain • low sensitivity if preconcentration is not used • adequate cleaning of containers between samples may be difficult
IX. Dinitrophenyl - hydrazine Liquid Impinger sampling using a Low-Volume Pump	HPLC/UV analysis	IV	• specific to aldehydes and ketones • good stability for derivatized compounds • low detection limits	• fragile equipment • sensitivity limited by reagent impurities • problems with solvent evaporation when long-term sampling is performed
X. Direct introduction by probe	Mobile MS/MS	I, II, III, IV	• immediate results • field identification of air contaminants • allows "real-time" monitoring • widest applicability of any analytical method	• high instrument cost • requires highly trained oeprators • grab samples only • no large data base on precision or accuracy

TABLE 12-13B. LIST OF COMPOUND CLASSES REFERENCED IN TABLE 12-13A

Category	Types of Compound
I	Volatile, nonpolar organics (e.g., aromatic hydrocarbons, chlorinated hydrocarbons) having boiling points in the range of 80 to 200°C.
II	Highly volatile, nonpolar organics (e.g., vinyl chloride, vinylidene chloride, benzene, toluene) having boiling points in the range of -15 to + 120°C.
III	Semivolatile organic chemicals (e.g., organochlorine pesticides and PCBs).
IV	Aldehydes and ketones.

TABLE 12-14. SAMPLING AND ANALYSIS TECHNIQUES APPLICABLE TO VAPOR PHASE ORGANICS

Compound Name	Whole Air	Tenax Cartridge TO-1	Carbon MS Cartridge TO-2	Cryogenic Trapping TO-3	Hi-Vol PUF TO-4	Liquid Impinger TO-5	NIOSH Method Number	Comments/Others
Acetophenone	X	X						
Acrolein	X					X		
Acrylonitrile	X		X	X				
Aniline	X			X			2002	
Arsenic and compounds							7900	Solid, use Std. Hi-Vol
Benzene	X	X	X	X				
Bis(2-ethylhexyl)phalate							5020	
Bromomethane	X		NP	X			2520	
Cadmium and compounds							7048	Solid, use Std. Hi-Vol
Carbon disulfide	X		NP	X			1600	
Carbon tetrachloride	X	B	X	X			1003	
Chlordane	X			X	X			
Chloroaniline (p)	NP			NP				No validated Method
Chlorobenzene	X	X		X			1003	
Chloroform	X	B	X	X			1003	
Chloromethane (methyl chloride)	X	B	NP		NP			
Chlorophenol								Needs XAD-2 Backup
Chloroprene (Neoprene)	X	X	NP	X			1002	
Chromium and compounds							7024	Solid, use Std. Hi-Vol
Copper cyanide							7029	Solid, use Std. Hi-Vol.

TABLE 12-14 (continued)

Compound Name	Whole Air	Tenax Cartridge TO-1	Carbon MS Cartridge TO-2	Cryogenic Trapping TO-3	Hi-Vol PUF TO-4	Liquid Impinger TO-5	NIOSH Method Number	Comments/Others
Cresol (o)							2001	Syn: methylphenol
Cresol (p)							2001	Syn: methylphenol
Cyanide	X						7904	
Dichloro-2-butene (1,4)	X	X		X				
Dichloro benzene (1,2)	X	X		X			1003	
Dichloro benzene (1,4)	X	X		X			1003	
Dichlorodifluoromethane	X	NP	NP					NIOSH 1012 should work
Dichloroethane (1,1) [ethylidine chloride]	X	X	NP	X			1003	
Dichlorophenoxyacetic acid (2,4)	X				NP		5001	Syn: 2,4-D
Dichloropropane (1,2)	X	X		X			1013	Method 1003 may be used
Dichloropropene (1,3)	X	NP		X				
Diethyl phthalate								No method identified
Dinotrotoluene (2,4)								Yellow crystals, use Hi-Vol
Dioxane (1,4)	X	X		X			1602	
Diphenylhydrazine (1,2)								No method identified
Ethylene dibromide	X	B		X			1008	Syn: 1,2-dibromoethane
Ethylene dichloride	X	B		X			1003	Syn: 1,2-dichloroethane
Fluorides							7902	Std. Hi-Vol for particulate fraction
Heptachlor								Waxy solid, use Std. Hi-Vol
Hexachlorobutadiene	X							

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TABLE 12-14. (continued)

Compound Name	Whole Air	Tenax Cartridge TO-1	Carbon MS Cartridge TO-2	Cryogenic Trapping TO-3	Hi-Vol PUF TO-4	Liquid Impinger TO-5	NIOSH Method Number	Comments/Others
Hexachloroethane		NP		X			1003	Syn: perchloroethane
Isobutanol		NP		X			1401	Syn: isobutyl alcohol
Lead and compounds							7802	Mostly particulate, use Hi-Vol
Mercury and compounds							7300	Mostly particulate, use Hi-Vol
Methacrylonitrile	X		NP	X				
Methyl ethyl ketone	X	X					2500	Syn: 2-butanone
Methyl methacrylate	X	NP		X				
Methylene chloride		B	X	X			1005	Syn: dichloromethane
Naphthalene	X				X		5515	Method TO-4 needs XAD-2
Nickel and compounds							7300	Mostly particulate, use Hi-Vol
Nitrobenzene	X	X		X			2005	
Nitrophenol	X	NP		X				
Parathion					NP		5012	
Pentachlorobenzene	X	NP		X				
Pentachloroethane	X	X		X				
Pentachlorophenol	X	NP						
Perchloroethylene	X	X		X				Syn. Tetrachloroethylene
Phenol	X	X		X			3502	
Phorate	X			X				
Pyridine	X							
Resorcinol	X							
Styrene	X	NP		X			1501	Syn. Polystyrene

TABLE 12-14. (continued)

Compound Name	Whole Air	Tenax Cartridge TO-1	Carbon MS Cartridge TO-2	Cryogenic Trapping TO-3	Hi-Vol PUF TO-4	Liquid Impinger TO-5	NIOSH Method Number	Comments/Others
TCDD (2,3,7,8)					X			
Toluene	X	X	X	X			1501	
Toxaphene	X				NP			Syn: Chlorinated camphene
Trichlorobenzene	X	NP		NP				
Trichloroethane (1,1,1)	X	B	X	X			1003	Syn: Methyl Chloroform
Trichloroethylene	X	X	X	X				
Trichloropropane (1,2,3)	X	X		X				
Vanadium pentoxide								Mostly particulate, use Hi-Vol
Vinyl acetate	X			X				
Vinyl chloride	X		X	X			1007	Syn: 1,1-dichloroethene
Vinylidene chloride (1,1 dichloroethylene)	X		X	X				
Xylene (m, o, p)	X	X		X			1501	Syn: dimethylbenzene
Zinc oxide							7530 and 7502	Solid, use Std. Hi-Vol

1. Blank spaces indicate that the method is inappropriate for that compound
2. B = small breakthrough volume for adsorbent
3. NP = not proven for this adsorbent, but may work
4. X = acceptable media for collection

TABLE 12-15

COMPOUNDS MONITORED USING EMSL-RTP TENAX SAMPLING PROTOCOLS

2-Chloropropane	1-Bromo-3-chloropropane
1,1-Dichloroethene	Ethylbenzene
Bromoethane	Bromoform
1-Chloropropane	Ethenylbenzene
Bromochloromethane	o-Xylene
Chloroform	1,1,2,2-Tetrachloroethane
Tetrahydrofuran	Bromobenzene
1,2-Dichloroethane	Benzaldehyde
1,1,1-Trichloroethane	Pentachloroethane
Benzene	4-Chlorostyrene
Carbon tetrachloride	3-Chloro-1-propene
Dibromomethane	1,4-Dichlorobutane
1,2-Dichloropropane	1,2,3-Trichloropropane
Trichloroethene	1,1-Dichloroethane
1,1,2-Trichloroethane	2-Chlorobutane
2,3-Dichlorobutane	2-Chloroethyl vinyl ether
Bromotrichloromethane	1,1,1,2-Tetrachloroethane
Toluene	p-Dioxane
1,3-Dichloropropane	Epichlorobutane
1,2-Dibromomethane	1,3-Dichlorobutane
Tetrachloroethene	p-Dichlorobenzene
Chlorobenzene	cis-1,4-Dichloro-2-butene
1,2-Dibromopropane	n-Butyl benzene
Nitrobenzene	3,4-Dichloro-1-butene
Acetophenone	1,3,5-Trimethyl benzene
Benzonitrite	
Isopropylbenzene	
p-Isopropyltoluene	

Sorbent techniques--A very common technique used to sample vapor-phase organics involves sorption onto a solid medium. Methods of this type usually employ a low- or high-volume pump to pull air through a glass tube containing the sorbent material. Organic compounds are trapped (removed from the air) by chemical attraction to the surface of the adsorbent material. After a predetermined volume of air has been pulled through the trap, the tube is capped and returned to the laboratory for analysis. Adsorbed organics are then thermally or chemically desorbed from the trap prior to GC or GC/MS analysis.

Thermal desorption is accomplished by rapidly heating the sorbent tube while a stream of inert gas flushes desorbed organics directly onto the GC column. Generally a secondary trap (either another sorbent or a cryogenically cooled loop) is used to hold the organics until injection into the GC column, but this step precludes multiple analyses of the sample.

Chemical desorption involves flushing the sorbent tube with an organic solvent, and analysis of the desorbed organics by GC or GC/MS. Since only a portion of the solvent is injected into the GC, sensitivity is lower than with thermal adsorption. However, reanalysis of samples is possible. The most common application of chemical desorption is for analysis of workplace air samples, where relatively high concentrations of organics are expected.

The primary advantages of sorbent techniques are their ease of use and ability to sample large volumes of air. Sorbent cartridges are commercially available for many applications, and can easily be adapted to portable monitoring pumps or personal samplers. A wide variety of sorbent materials are available, and sorbent traps can be used singly or in series for maximum retention of airborne pollutants. Sorbent methods are especially applicable to integrated or long-term sampling, because large volumes of air can be passed through the sampling tube before breakthrough occurs.

In choosing a sorbent method, the advantages and limitations of specific methods should be considered along with general limitations of sorbents. Some important considerations are discussed below.

- Sorbents can be easily contaminated during manufacturing, shipping or storage. Extensive preparation (cleaning) procedures are generally needed to insure that the sorbent is free from interfering compounds prior to sampling. Tenax, for example, is often contaminated with benzene and toluene from the manufacturing process, requiring extensive solvent extraction and thermal conditioning before it is used. Once prepared, sampling cartridges must be protected from contamination before and after sampling.

- No single adsorbent exists that will retain all vapor phase organics. The efficiency of retention of a compound on a sorbent depends on the chemical properties of both compound and sorbent. Generally, a sorbent that works well for nonpolar organics such as benzene will perform poorly with polar organics such as methanol, and vice versa. Highly volatile compounds such as vinyl chloride will not be retained on weakly adsorbing materials such as Tenax, while less volatile compounds will be irreversibly retained on strong adsorbents such as charcoal. The optimal approach involves use of a sorbent that will retain a wide range of compounds with good efficiency, supplemented by techniques specifically directed towards "problem" compounds.

- Tenax-GC is a synthetic polymeric resin which is highly effective for volatile nonpolar organics such as aliphatic and aromatic hydrocarbons, and chlorinated organic solvents. Table 12-15 lists compounds that have been successfully monitored using a Tenax sorption protocol. Tenax has the important advantage that it does not retain water. Large amounts of water vapor condensing on a sorbent reduces collection efficiency and interferes with GC and GC/MS analysis. Another advantage of this material is the ease of thermal or chemical desorption.

  The major limitation of Tenax is that certain highly volatile or polar compounds are poorly retained (e.g., vinyl chloride, methanol). Formation of artifacts (i.e., degradation products from the air contaminant sample collected due to hydrolysis, oxidation, photolysis or other processes) on Tenax has also been noted, especially the oxidation

of amines to form nitrosamines, yielding false positive results for the latter compounds.

Carbon sorbents include activated carbon, carbon molecular sieves, and carbonaceous polymeric resins. The major advantage of these materials is their strong affinity for volatile organics, making them useful for highly volatile compounds such as vinyl chloride. The strength of their sorptive properties is also the major disadvantage of carbon sorbents because some organic compounds may become irreversibly adsorbed on the carbon. Thermal desorption of compounds with boiling points above approximately 80°C is not feasible due to the high temperature (400°C) required. Carbon adsorbents will retain some water, and therefore may not be useful in high humidity conditions.

In addition to the Tenax and carbon tube sampling methods shown above, passive sorption devices for ambient monitoring can be used. These passive samplers consist of a portion of Tenax or carbon held within a stainless steel mesh holder. Organics diffuse into the sampler and are retained on the sorbent material. The sampling device is designed to fit within a specially constructed oven for thermal desorption. Results from these passive samplers were reported to compare favorably with pump-based sorbent techniques. Because of the difficulty of determining the volume of air sampled via passive sampling, these devices would appear to be mainly applicable for screening purposes.

- Polyurethane foam (PUF) has been used extensively and effectively for collection of semivolatile organics from ambient air. Semivolatiles include PCBs and pesticides. Such compounds are often of concern even at verly low concentrations. A significant advantage of PUF is its ability to perform at high flow rates, typically in excess of 500 liters per minute (l/m). This minimizes sampling times.

  PUF has been shown to be effective for collection of a wide range of semivolatile compounds. Tables 12-16 and 12-17 list compounds that have been successfully quantified in ambient air with PUF. Compounds

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TABLE 12-16. SUMMARY LISTING OF ORGANIC COMPOUNDS SUGGESTED FOR COLLECTION WITH A LOW VOLUME POLYURETHANE FOAM SAMPLER AND SUBSEQUENT ANALYSIS WITH AN ELECTRON CAPTURE DETECTOR (GC/ECD)[a]

Polychlorinated Biphenyls (PCBs)

Aroclor 1221[c]
Aroclor 1232[d]
Aroclor 1242[a]
Aroclor 1016[c]
Aroclor 1248[d]
Aroclor 1254[a]
Aroclor 1260[a]

Chlorinated Pesticides

α-chlordane[a]
Y-chlordane[a]
Chlordane (technical)[a]
Mirex[a]
α -BHC[a]
β-BHC[d]
-BHC (Lindane)[a]
-BHC[d]
p,p'-DDD[d]
p,p'-DDE[a]
p, p'-DDT[a]
Endosulfan I[a]
Heptachlor[d]
Aldrin[a]

Polychlorinated Napthalenes (PCNs)

Halowax 1001[c]
Halowax 1013[c]

Chlorinated Benzene

1,2,3-Trichlorobenzene[a]
1,2,4-Trichlorobenzene[d]
1,3,5-Trichlorobenzene[d]
1,2,3,4-Tetrachlorobenzene[a]
1,2,3,5-Tetrachlorobenzene[d]
1,2,4,5-Tetrachlorobenzene[d]
Pentachlorobenzene[a]
Hexachlorobenzene[a]
Pentachloronitrobenzene[a]

Chlorinated Phenols

2,3-Dichlorophenol[b]
2,4-Dichlorophenol[b]
2,5-Dichlorophenol[b]
2,6-Dichlorophenol[b]
3,4-Dichlorophenol[b]
3,5-Dichlorophenol[b]
2,3,4-Trichlorophenol[d]
2,3,5-Trichlorophenol[d]
2,3,6-Trichlorophenol[d]
2,4,5-Trichlorophenol[a]
2,4,6-Trichlorophenol[d]
3,4,5-Trichlorophenol[d]
2,3,4,5-Tetrachlorophenol[d]
2,3,4,6-Tetrachlorophenol[d]
2,3,5,6-Tetrachlorophenol[d]
Pentachlorophenol[a]

a Method validation data for all components, unless otherwise noted, are available in the literature. This includes collection efficiency data and/or retention efficiency data, method recovery data, and in some cases, storage stability data on selected isomers from this compound class.

b Method validation data not presently available in the literature for either a low or high volume sampling procedure. Dichlorophenols, however, are amenable to the same analytical protocols suggested for the higher molecular weight clorophenol isomers (trichloro, tetrachloro, and pentachloro). Users are cautioned that sample collection efficiencies may not be as high for dichlorophenols as for the higher molecular weight chlorophenols. Collection/retention efficiency data should be generated for each specific program.

c Validation data employing low volume sampling conditions not presently available in literature. Component has, however, been evaluated using high volume PUF sampler.

d Actual validation data for isomer(s) employing low volume PUF sampler not available in literature. Behavior under low volume sample conditions should be similar to other structural isomers listed. Component is amenable to analytical scheme employing GC/ECD.

TABLE 12-17. SUMMARY LISTING OF ADDITIONAL ORGANIC COMPOUNDS SUGGESTED FOR COLLECTION WITH A LOW VOLUME POLYURETHANE FOAM SAMPLER

Polynuclear Aromatic Hydrocarbons[a]	Herbicide Esters	Urea Pesticides
Napthalene	2,4-D Esters, isopropyl[c]	Monuron[c]
Biphenyl	2,4-D Esters, butyl[c]	Diuron[c]
Fluorene	2,4-D Esters, isobutyl[c]	Linuron[c]
Dibenzothiophene	2,4-D Esters, isooctyl[c]	Terbuthiuron[c]
Phenanthrene		Fluometuron[c]
Anthracene	**Organophosphorous Pesticides**	Chlorotoluron[c]
Carbazole		
2-Methylanthracene	Mevinphos[b]	**Triazine Pesticides**
1-Methylphenanthrene	Dichlorvos[c]	
Fluoranthene	Ronnel[c]	Simazine[c]
Pyrene	Chlorpyripos[c]	Atrazine[c]
Benzo(a)fluorene	Diazinon[c]	Propazine[c]
Benzo(b)fluorene	Methyl parathion[c]	
Benzo(a)anthracene	Ethyl parathion[c]	**Pyrethrin Pesticides**
Chrysene/triphenylene		
Benzo(b)fluoranthene	**Carbamate Pesticides**	Pyrethrin I[c]
Benzo(e)pyrene		Pyrethrin II[c]
Benzo(a)pyrene	Propoxur[c]	Allethrin[c]
Perylene	Carbofuran[c]	d-trans-Allethrin[c]
o-Phenylenepyrene	Bendiocarb[c]	Dicrotophos[c]
Dibenzo(ac)/(ah)anthracene	Mexacarbate[c]	Resmethrin[c]
Benzo(g,h,i)perylene	Carbaryl[c]	Fenvalerate[c]
Coronene		

a These components have been reported in the literature using polyurethane foam samplers. Users are cautioned that this listing is provided solely as a working reference. Method validation studies including collection efficiencies, retention efficiencies, etc., employing the sampling procedures cited in this document have not been conducted. Procedures other than those noted in this document may be more applicable in routine use.

b Validation data employing low volume sampling conditions not presently available in literature. Component, however, has been evaluated using high volume PUF sampler.

c Sample evaluation data for these compound classes using a low volume PUF sampler contained in the literature.

that have shown poor retention or storage behavior with PUF include hexachlorocyclohexane, dimethyl and diethylphthalates, mono- and dichlorophenols, and trichloro- and tetrachlorobenzenes. These compounds have higher vapor pressures, and may be collected more effectively with Tenax or with resin sorbents such as XAD-2.

PUF is easy to handle, pre-treat, and extract. Blanks with very low contaminant concentrations can be obtained, as long as precautions are taken against contamination after pretreatment. Samples have been shown to remain stable on PUF during holding times of up to 30 days. PUF concentration methods have shown excellent collection efficiency and recovery of sorbed compounds from the material.

Most PUF methods specify the use of a filter ahead of the PUF cartridge, to retain particulates. The filter prevents plugging of the PUF which would reduce air flow through the sorbent. Some methods recommend extracting the filter separately to obtain a value for particulate organics. However, because most semivolatile compounds have sufficient vapor pressure to volatilize from the filter during the collection period, particulate measurements may not be representative of true particulate concentrations. Therefore, results from the PUF analyses may overestimate gaseous concentrations of semi-volatile compounds due to volatilization of semi-volatiles originally collected on the sampler inlet filter and subsequently collected by the PUF cartridge.

- Cryogenic methods for capturing and collecting volatile organics involve pulling air through a stainless steel or nickle U-tube immersed in liquid oxygen or liquid argon. After sampling, the tube is sealed, stored in a coolant, and returned to the laboratory for anlaysis. The trap is connected to a GC, rapidly heated, and flushed into a GC or GC/MS for analysis.

The major advantage of cryogenic concentration is that all vapor phase organics, except the most volatile, are concentrated. This is a distinct advantage over sorbent concentration, which is especially selective for particular chemical

classes. Contamination problems are minimal with cryogenic methods because a collection media is not required.

Several disadvantages limit the current usefulness of cryogenic methods, including:

- Samplers rapidly become plugged with ice in high humidity conditions. This limits the volume of air that can be sampled.

- The entire sample is analyzed at once, enhancing sensitivity but making multiple analyses of a sample impossible.

- The necessity of handling and transporting cryogenic liquids makes this method cumbersome for many sampling applications.

- There is a possibility of chemical reactions between compounds in the cryogenic trap.

Whole air sampling--Air may be collected without preconcentration for later use in direct GC analysis or for other treatment. Samples may be collected in glass or stainless steel containers, or in inert flexible containers such as Tedler bags. Rigid containers are generally used for collection of grab samples, while flexible containers or rigid containers may be used to obtain integrated samples. Using a flexible container to collect whole air samples requires the use of a sampling pump with flow rate controls. Sampling with rigid containers is performed either by evacuating the container and allowing ambient air to enter, or by having both inlet and outlet valves remain open while pumping air through the container until equilibrium is achieved.

Whole air sampling is generally simple and efficient. Multiple analyses are possible on samples, allowing for good quality control. This method also has the ability to be used for widely differing analyses on a single sample. The method has been widely used, and a substantial data base has been developed.

Problems may occur using this method due to decomposition of compounds during storage and loss of some organics by adsorption to the container walls.

Sample stability is generally much greater in stainless steel containers than in glass or plastic. Whole-air sampling is limited to relatively small volumes of air (generally up to 20 liters due to the impracticality of handling larger sample collection containers), and has higher detection limits than some sorbent techniques.

Impinger collection--Impinger collection involves passing the air stream through an organic solvent. Organics in the air are dissolved in the solvent, which can then be analyzed by GC/MS. Large volumes of air sampled cause the collection solvent to evaporate. In addition, collection efficiency is dependent on flow rate of the gas, and on the gas-liquid partition coefficients of the individual compounds. However, there are certain specialized applications of impinger sampling that have been found to be preferable to alternate collection techniques (e.g., sampling for aldehydes and ketones).

Certain compounds of interest are highly unstable or reactive, and will decompose during collection or storage. To concentrate and analyze these compounds, they must be chemically altered (derivatized) to more stable forms. Another common reason for derivatization is to improve the chromatographic behavior of certain classes of compounds (e.g., phenols). Addition of the derivatization reagent to impinger solvent is a convenient way to accomplish the necessary reaction.

A widely used method for analysis of aldehydes and ketones is a DNPH (dinitrophenylhydrazine) impinger technique. Easily oxidized aldehydes and ketones react with DNPH to form more stable hydrazone derivatives, which are analyzed by high performance liquid chromatography (HPLC) with a UV detector. This method is applicable to formaldehyde as well as less volatile aldehydes and ketones.

Direct analysis--A method not requiring preconcentration or separation of air components is highly desirable, because it avoids component degradation or loss during storage. Air is drawn through an inert tube or probe directly into the instrument detector. Several portable instruments exist that can provide direct air analysis, including infrared spectrophotometers, mobile MS instruments, and portable FID detectors. Some of these instruments have been discussed in the section on screening methods.

Mobile mass spectrometry has been used to compare upwind and downwind concentrations of organic pollutants at hazardous waste management facilities. The advantage of the multiple mass spectrometer configuration (MS/MS or triple MS) over a single MS system is that multiple systems can identify compounds in complex mixtures without pre-separation by gas chromatography. Major limitations of MS/MS methods are low sensitivity and high instrument cost.

In summary, of the methods described in this subsection, the majority of vapor-phase organics can be monitored by use of the following sampling methods:

- Concentration on Tenax or carbon adsorbents, followed by chemical or thermal desorption onto GC or GC/MS.
- Sorption on polyurethane foam (PUF) cartridges, followed by solvent extraction.
- Cryogenic trapping in the field.
- Whole-air sampling.

12.8.2.2.1.2 Particulate Organics

Certain hazardous organic compounds of concern in ambient air are primarily associated with airborne particles, rather than in the vapor phase. Such compounds include dioxins, organochlorine pesticides, and polyaromatic hydrocarbons. Therefore, to measure these compounds accurately, it is necessary to monitor particulate emissions from units of concern.

Measurement of particulate organics is complicated because even relatively nonvolatile organics exhibit some vapor pressure, and will volatilize to a certain extent during sampling. The partitioning of a compound between solid and gaseous phases is highly dependent on the sampling conditions (e.g., sampling flow rate, temperature). Particulate sampling methods generally include a gas phase collection device after the particulate collector to trap those organics that become desorbed during sampling.

The most common methods used for collection of particles from ambient air are:

- Filtration
  - Cellulose Fiber
  - Glass or Quartz Fiber
  - Teflon Coated Glass Fiber
  - Membranes
- Centrifugal Collection (e.g., cyclones)
- Impaction
- Electrostatic Preciptation

The standard sampling method for particulates is filtration. Teflon-coated glass membranes generally give the best retention without problems with separating the particulates sampled from the filter. Problems, however, may be caused by desorption of organics from the filter, by chemical transformation of organics collected on the filter, and with chemical transformation of organics due to reaction with atmospheric gases such as oxides of nitrogen and ozone. These problems are magnified by the large volumes of air that must be sampled to obtain sufficient particulate material to meet analytical requirements. For example, to obtain 50 milligrams of particulates from a typical air sample, 1000 cubic meters of air must be sampled, involving about 20 hours of sampling time with a high-volume sampling pump.

Despite the drawbacks mentioned above, filtration is currently the simplest and most thoroughly tested method of collecting particulates for organic analysis. Other methods, such as electrostatic precipitation, make use of electrical charge or mechanical acceleration of the particles. The effect of these procedures on compound stability is poorly understood.

12.8.2.2.2 Monitoring Inorganic Compounds in Ambient Air

12.8.2.2.2.1 Particulate Metals

Metals in ambient air can occur as particulates or can be adsorbed on other particulate material. Metals associated with particulate releases are effectively collected by use of filter media allowing for the collection of adequate samples for analysis of a number of particulate contaminants.

Collection on filter media--Sampling methods for particulate metals are generally based on capture of the particulate on filter media. For the most part, glass fiber filters are used; however, organic and membrane filters such as cellulose ester and Teflon can also be used. These membrane filters demonstrate greater uniformity of pore size and, in many cases, lower contamination levels of trace metals than are found in glass fiber filters. Analytical procedures described in the following reference can be utilized to analyze particulate samples.

U.S. EPA. 1986. Test Methods for Evaluating Solid Waste. 3rd Edition. EPA SW-846. GPO No. 955-001-00000-1. Office of Solid Waste. Washington, D.C. 20460.

Hi-Vol collection devices--The basic ambient air sampler is the high volume sampler which can collect a 2000 cubic meter sample over a 24-hour period and capture particulates on an 8 x 10 inch filter (glass fiber) as described in 40 CFR Part 50. It has a nominal cut point of 100μm for the maximum diameter particle size captured. A recent modification involves the addition of a cyclone ahead of the filter to separate respirable and non-respirable particulate matter. Health criteria for particulate air contaminants are based on respirable particulate matter.

Personnel samplers--Another particulate sampling method involves the use of personnel samplers according to NIOSH methods (NIOSH, 1984). The NIOSH methods are intended to measure worker exposure to particulate metals for comparison to OSHA standards. A 500-liter air volume is sampled at approximately 2 liters per minute. This method is most efficient when less than 2 mg total particulate weight are captured. Capture of more than 2 mg may lead to sample

losses during handling of the sample. The preferred filter medium is cellulose ester (47 mm diameter) which will dissolve during the standard acid digestion.

The NIOSH method, however, is not recommended for the RFI for several reasons. The NIOSH analytical methods (and good QA/QC practices) require several aliquots of the sample to be prepared for best analytical results. The 47 mm filter is too small for aliquoting; therefore, use of the NIOSH method would require the simultaneous operation of several sampling systems. More importantly, the 500 liter sample volume generally does not provide sufficient particulate matter for the analytical methods to detect trace ambient levels of metals. The method is best suited for industrial hygiene applications.

Dichotomous Samplers--Dichotomous samplers (virtual impactors) have been developed for particle sizing with various limit cutpoints for use in EPA ambient monitoring programs. These samplers collect two particulate fractions on separate 37 mm diameter filters from a total air volume of about 20 cubic meters. The standard sampling period is 24 hours. Teflon filters are generally recommended by sampler manufacturers because they exhibit negligible particle penetration and result in a low pressure drop during the sampling period. However, glass fiber and cellulose filters are also acceptable.

The need for multiple extractions would require multiple sampling trains. If the two filters are combined to form one aliquot and extracted together, they will provide sufficient sensitivity for some but not all analytical procedures and defeat the purpose of fractioning the sample. The use of the dichotomous sampler is, therefore, limited.

12.8.2.2.2.2 Vapor Phase Metals

Most metallic elements and compounds have very low volatilites at ambient temperatures. Those that are relatively volatile, however, require a different sampling method than used for collection of particulate forms, although analytical techniques may be similar. For the purpose of ambient monitoring, vapor-phase metals are defined as all elements or compounds that are not effectively captured by standard filter sampling procedures. Available methods for the measurement of vapor phase metals are presented in Tables 12-18 and 12-19. These available

TABLE 12-18. SAMPLING AND ANALYSIS METHODS FOR VOLATILE MERCURY

Method/Reference	Species measured	Procedures summary	Advantages	Disadvantages
NIOSH P&CAM 6000	Particulate, organic and elemental mercury	Sampling train consists of membrane filter to capture particulate Hg, followed by Carbosieve B to trap organic Hg, and then silver coated Chromosorb P (CP) to collect elemental Hg. Each section is analyzed separately by thermal desorption into a flameless AA. Filters are acid digested, reduced to Hg and amalgamated on Ag CP prior to the AA analysis step.	- Standard method - Permits measurement of all three types of mercury - Method selective to mercury	- Requires use of complex desorption unit - Cl_2 interferes with sampling - Separation of organic and metallic mercury is uncertain at 0.001 Hg/total Hg - Requires preparation of special sorbents
NIOSH SCP-S342	Organic mercury	Filter to separate particulate; adsorb organic Hg on Carbosieve B; thermally desorb into flameless AA unit	- Standard method - Option to P&CAM 175 if organic mercury is only concern - Range is 20-80 $\mu g/m^3$ with a 3 liter sample volume	- Requires complex thermal desorption unit
EPA Method 101	Particulate and vaporous mercury	Collection in acidified 0.1 N HCl impinger solution; analysis by NAA or optionally by cold vapor AA	- Standard method - Detection limit of 1 $\mu g/m^3$ - Fairly stable reagent - Same reagent has been used for volatile Pb (Ref. 572)	- NAA expensive and not routinely available - Ice interferes with cold vapor AA method at low concentrations of Hg - Instability of collected Hg compounds in solution has been reported
Canadian EPS Standard Method	Particulate and vaporous mercury	Collection in impinger solution of 10% H_2SO_4/2% $KMnO_4$; analysis by cold vapor AA	- Standard method - Collection efficiency $\geq 90\%$ - $KMnO_4$ and AA compatible - AA costs $\approx \$30$/sample - Reagent gives low blank levels	- $KMnO_4$ reagent must be prepared within 12 hours of use - Short sample holding time - Reagent can be easily expended in oxidizing and organic matrices

TABLE 12-18. (continued)

Method/Reference	Species measured	Procedures summary	Advantages	Disadvantages
Environment Canada	Vaporous mercury or particulate mercury	Vaporous mercury is collected by amalgamation on silver. Particulate is collected on microquartz filters. Both are analyzed by thermal desorption and/or pyrolysis with re-amalgamation; then thermal desorption for determination by UV absorption at 253.7	- Standard method for ambient air - Used in range of 4-22 mg/m^3 - Claimed to be "inexpensive"	- Complex desorption/amalgamation unit
3M Badge	Elemental Hg vapor	Passive device-diffusion of Hg through membrane, amalgamation on gold, analysis of badges performed by 3M	- Very simple and mercury specific method - Requires no analysis to be performed by users - Gives 8-hour time weighted average and concentrations of up to 20 μg/m^3	- Cl_2 interferes with sampling efficiency - High H_2S and SO_2 also interfere - Temperature variations affect diffusion rates and must be corrected for
MSA Method	Elemental and organic mercury	Adsorb mercury on iodine impregnated charcoal; place in tantalum boat and volatilize	- Simple equipment requirements - Range of 50-200 μg/m^3 tested	- Large coefficient of variation - Quality of results are very much operator dependent - Only works well at 200 μg/m^3
Hopcalite Method	Elemental and organic mercury	Adsorb on hopcalite; dissolve sorbent and mercury in HNO_3 + HCl; analyze by cold vapor AA	- Simple equipment requirement - Evaluated in range of 50-200 μg/m^3	- Does not provide for analysis of particulate mercury - Insufficient performance data in available literature

TABLE 12-18 (continued)

Method/Reference	Species measured	Procedures summary	Advantages	Disadvantages
Silver amalgamation and APHA	Vaporous elemental mercury	Amalgamation on silver wool or silver gauge; thermal desorption with analysis by flameless AA or UV absorption	- Substantial information on the method; interferences provided in the references - Ag wool-24 hour sample can be used with 15 ng-10 pg/m^3 levels - Ag gauge ≤ 2 hour sample can give concentrations of 5 ng-100 μg/m^3	- Collection efficiency for organic mercury is in question - Oxidants could interfere with sampling procedure unless removed before reaching silver
Impinger/Dithizone	Organic, particulate and vaporous mercury	Collect in impinger solution of 0.1 NiCl and 0.5 m HCl; analyze by the dithizone colorimetric method	- Efficient capture of all three types of volatile mercury	- Dithizone method suffers from high blanks, interference from SO_2 and interference from several other metals - Mercury compounds collected in HCl are unstable
Jerome Instrument Corp., Model 411, Gold Film Hg Vapor Analyzer	Elemental mercury	Onsite monitor-amalgamation of Hg on gold, measure concentration by change in gold foil resistance	- Selective for mercury - Direct reading eliminates sample transport and analysis - Concentration range from μg/m^3 to mg/m^3	- Monitor costs $3500-$4000 - May suffer interference from oxidants as noted for 3M badges

• Recommended methods

TABLE 12-19. SAMPLING AND ANALYSIS OF VAPOR STATE TRACE METALS (EXCEPT MERCURY)

Element	Reference(s)	Species measured	Procedures summary	Advantages	Disadvantages
Antimony	NIOSH S243	Stibine (SbH_3)	Adsorb on mercuric chloride impregnated silica gel; extract with concentration HCl; oxidize Sb(111) to Sb(V) with ceric sulfate; colorimetric analysis by Rhodamine	- Standard method	- Range only 0.1-1.0 ng/m^3 using a 20-liter sample - Analytical interferences by Pb(III), Tl(I), and Sb(II)
Arsenic	NIOSH P&CAM 6001	Arsine (AsH_3)	Adsorb on charcoal; desorb with HNO_3; analyze by furnace AA	- Standard method	- Possible breakthrough at high concentrations
	NIOSH S229 NIOSH 7900	Arsine (AsH_3)	Same as P&CAM 265 except that HNO_3 desorption is performed with 10 ml rather than 1 ml	- Standard method - Working range 0.09-0.1 mg/m^3	- Possible breakthrough at high concentrations - Earlier version of P&CAM 265
		As_2O_3 and others	Absorb in dilute NaOH solution; analytical procedure not specified but it may be suitable to use arsine generation or furnace AA	- Only method proposed for AS_2O_3 in available literature - Relatively simple	- No supporting data available
*Lead	NIOSH S383 and S384	Tetraethyl lead and tetramethyl lead	Adsorb on XAD-2; desorb with pentane; analysis by GC	- Standard method - Permits separation of the various alkyl lead compounds - Range 0.045-0.20 ng/m^3 (as Pb) - Can alter GC conditions to remove interferences with analysis	- Compound identification only by GC retention times; must verify
		Alkyl lead compounds	Collect in HCl/NiCl impinger solution; analyze by dithizone colorimetric method when 8-hour sampling period or by AA for 24 hour sample	- Near 100% collection efficiency - Dithizone detection limit - 10 µg/m^3 - AA detection limit - 0.2 - 10 µg/m^3	- Very little information in literature - Dithizone method may have same problems noted elsewhere for other elements

TABLE 21-19. (continued)

Element	Reference(s)	Species measured	Procedures summary	Advantages	Disadvantages
		Alkyl lead compounds	Adsorb on activated carbon; digest with HNO_3 + $HClO_4$; analyze by dithizone method	- Good collection efficiency - Low detection limits possible	- No data available - Dithizone method may have interferences as noted above
Nickel	NIOSH P&CM 344	Nickel tetracarbonyl ($Ni(CO)_4$)	Adsorb on charcoal; desorb with dilute HNO_3; analyze by furnace AA	- Standard method - AA specific for Nickel - Range 2-60 $\mu g/m^3$	- Sorbent capacity limits upper concentration
	Ref. 120, 142	Nickel tetracarbonyl ($Ni(CO)_4$)	Absorb in 3% HCl impinger solution; analyze by colorimetric method in which color development in chloroform phase is measured	- Detection limit - 0.001 ppm	- Not a standard method - Interference may occur from other Nickel compounds, Cu, Pb, Cr, Se and V
Selenium		SeO_2, H_2SeO_3	Collect in impinger with aqueous solution of Na_2SO_3, Na_2S, or NaOH, analyze by NAA, AA, GC, colorimetry, fluorimetry, ring oven techniques, or catalytic methods	- Only method suggested in literature for volatile Se	- No data to support this method

methods are generally developed for industrial hygiene applications by NIOSH.

The methods for measuring vapor-phase metals presented in Tables 12-18 and 12-19 have undergone limited testing for precision and accuracy and have had matrix interferences documented. Therefore, they should be used in lieu of any methods which have no supporting data.

Several methods are suitable for quantification of vapor-phase mercury. If elemental mercury is to be measured, the silver amalgamation technique with thermal desorption and flameless AA (atomic absorption) analysis is recommended. This technique is presented in American Public Health Association (APHA) Method 317, which can achieve nanogram per cubic meter detection limits. If organic and/or particulate mercury are also to be determined, NIOSH methods (NIOSH, 1984) are recommended. These methods can measure all three airborne mercury species, but require a complex two stage thermal desorption apparatus.

12.8.2.2.2.3 Monitoring Acids and Other Compounds in Air

Monitoring for acids and other inorganic/non-metal compounds (e.g., hydrogen sulfide) in the ambient air will generally require application of industrial hygiene technologies. Applicable methods have been compiled in the following references:

NIOSH. February 1984. NIOSH Manual of Analytical Methods. NTIS PB 85-179108. National Institute for Occupational Safety and Health. Cincinnati, OH.

ASTM. 1981. Toxic Materials in the Atmosphere. ASTM, STP 786. Philadelphia, PA.

APHA. 1977. Methods of Air Sampling and Analysis. American Public Health Association.

ACGIH. 1983. Air Sampling Instruments for Evaluation of Atmospheric Contamination. American Conference of Governmental Industrial Hygienists. Cincinnati, OH.

12.8.3 Stack/Vent Emission Sampling

EPA methods for source-sampling and analysis are documented in the following reference:

Code of Federal Regulations. 40 CFR Part 60, Appendix A: Reference Methods. Office of the Federal Register, Washington, D.C.

Additional guidance is available in the following references:

U.S. EPA. 1978. Stack Sampling Technical Information, A Collection of Monographs and Papers, Volumes I-III. EPA-450/2-78-042 a, b, c. NTIS PB 80-161672, 80-1616680, 80-161698. Office of Air Quality Planning and Standards Research Triangle Park, NC 27711.

U.S. EPA. February 1985. Modified Method 5 Train and Source Assessment Sampling System Operators Manual. EPA-600/8-85-003. NTIS PB 85-169878. Office of Research and Development. Research Triangle Park, NC 27711.

U.S. EPA March 1984. Protocol for the Collection and Analysis of Volatile POHC's Using VOST. EPA-600/8-84-007. NTIS PB 84-177799. Office of Research and Development. Research Triangle Park, NC 27711.

U.S. EPA. February 1984. Sampling and Analysis Methods for Hazardous Waste Combustion. EPA-600/8-84-002. NTIS PB 84-155845. Washington, D.C. 20460.

U.S. EPA. November 1985. Practical Guide - Trial Burns for Hazardous Waste Incinerators. NTIS PB 86-190246. Office of Research and Development. Cincinnati, OH 45268.

U.S. EPA. 1981. Source Sampling and Analysis of Gaseous Pollutants. EPA-APTI Course Manual 468. Air Pollution Control Institute. Research Triangle Park, NC 27711.

U.S. EPA. 1979. Source Sampling for Particulate Pollutants. EPA-APTI Course Manual 450. NTIS PB 80-188840, 80-174360, 80-182439. Air Pollution Control Institute. Research Triangle Park, NC 27711.

U.S. EPA. 1986. Test Methods for Evaluating Solid Waste. 3rd Edition. EPA/SW-846. GPO No. 955-001-00000-1. Office of Solid Waste. Washington, D.C. 20460.

12.8.3.1 Vapor-Phase and Particulate Associated Organics

Generally, point source vapor-phase samples are obtained from the process vents and effluent streams either by a grab sample technique or by an integrated sampling train. Careful planning is necessary to insure that sampling and analytical techniques provide accurate quantitative and qualitative data for measurement of vapor-phase organics. Considerations such as need for real-time (continuous) versus instantaneous or short-term data, compatibility with other compounds/parameters to be measured, and the need for onsite versus offsite analysis may all be important in the selection process.

Monitoring for complex organic compounds generally requires detailed methods and procedures for the collection, recovery, identification, and quantification of these compounds. The selection of appropriate sampling and analytical methods depends on a number of important considerations, including source type and the compounds/parameters of interest. Table 12-20 lists several sampling methods for various applications and compound classess (applicable to combustion sources). The first three methods listed are fixed-volume, grab-sampling methods. Grab sampling is generally the simplest technique to obtain organic emission samples.

Sample collection by the bag and canister sampling methods can be used to collect time-integrated samples. These methods also allow for a choice of sample volumes due to a range of available bag sized (6, 12, and 20 liter capacities are typical). Bags of various materials are available, including relatively inert and noncontaminating materials such as Teflon, Tedlar, and Mylar. All sample collection bag types may have some sample loss due to adsorption of the contaminants collected to container walls. The bag sample is collected by inserting the bag into

TABLE 12-20. SAMPLING METHODS FOR TOXIC AND HAZARDOUS ORGANIC MATERIALS FROM POINT SOURCES

Sampling Method	Description	Applicable Source Type	Applicable Compound Type	Applicable Analytical Method(s)	Sampling Method Limitations
Syringe Flow-through bottle Evacuated canister Tedlar bag (EPA Method 3)	Instantaneous grab Instantaneous grab Integrated grab Integrated grab	Non-combustion (storage tanks spray booths paint bake ovens, etc.) Low moisture content combustion emissions (boilers, incinerators, etc.).	Volatiles, C_1-C_{10} Volatiles, C_1-C_{10} Volatiles, C_1-C_{10} Volatiles, C_1-C_{10}	GC-FID[a] GC-MS[b] or GC-PID[c]	Sample size and therefore detectable concentration are limited by container size; ≥ 1 ppm. Bag samples are subject to absorptive losses of sample components.
EPA method 25	Two stage integrated grab train consisting of cold trap followed by evacuated S.S. tank.	Non-combustion and low moisture content combustion emissions as above.	Volatiles and semi-volatiles, C_1-C_{16}	Oxidation/ reduction followed by GC/FID.	Sample size is limited by tank volume. CO_2 and H_2O can produce significant interferences. System is complex/cumbersome.
VOST[d]	Water-cooled sample gas, including condensate, is passed through dual in-series sorbent traps. Tenax GC in first tube followed by Tenax GC backed-up by charcoal in second tube.	Combustion emissions (boilers, hazardous waste incinerators, etc.).	Volatiles and semi volatiles, C_1-C_{16}· C_1-C_{10}	GC-MS GC-ECD GC-PID	Sample size is limited to 20 liters per pair of sorbent tubes. Sorbent tubes are susceptable to contamination from organics in ambient air during installation and removal from train.

TABLE 12-20 (continued)

Sampling Method	Description	Applicable Source Type	Applicable Compound Type	Applicable Analytical Method(s)	Sampling Method Limitations
Modified Method 5	Water-cooled sample gas, with condensate is passed through single sorbent trap. Sorbent type dependent on compound(s) of interest.[e]	Combustion emission as for VOST.	Semi-volatiles, PCB's, other halogenated organics, C_7-C_{16}, C_1-C_{10}	GC-ECD, GC-HECD, GC-MS	Single trap system does not provide check for breakthrough. Flow rate limited to approximately 1 cpm.
High Volume Modified Method 5	Sample gas is passed through condensers where moisture is removed before passing through two sorbent traps, primary followed by back-up. Flow rates of up to 5 cpm are achievable. Sorbent type dependent on compounds of interest.[e]	Combustion emissions.	Semi-volatiles, PCBs, other halogenated organics, C_7-C_{16}, C_1-C_{10}	GC-ECD, GC-HECD, GC-MS	High flow rate results in high sampling train pressure drop requiring large pump capacity.
SASS Train	Sample gas passes through a cold trap followed by an XAD-2 sorbent trap. Train is all stainless steel construction.	Combustion emissions (boilers, hazardous waste incinerators).	Semi-volatiles, and other, non-halogenated organics, C_7-C_{16}	GC-ECD, GC-HECD, GC-MS	System is complex, large and cumbersome. Recovery of organics from cold trap can be difficult. S.S. construction makes train components highly susceptable to corrosion from acidic gases especially HCl.

a GC-FID - gas chromatography with flame ionization detector.
b GC-MS - gas chromatography-mass spectrometry.
c GC-PID - gas chromatography-photoionization detector.
d VOST - volatile organic sampling train.
e Sorbents include Florisil, XAD-2 resin, and Tenax-GC among the most commonly used.

Source: Hazardous Waste Management, Vol. 35, No. 1, January 1985

an airtight, rigid container (lung) and evacuating the container. The sample is drawn into the bag because reduced pressure in the container provides adequate suction to fill the bag. This procedure is presented in detail in 40 CFR Part 60, Appendix A (Method 3).

Evacuated canisters are conventionally constructed of high grade polished stainless steel. There are many versions available ranging from units with torque limiting needle valves, purge free assemblies, internal electropolished surfaces and versions utilizing stainless steel beakers with custom designed tops and fittings. Also, different container materials may react differently with the sample. Therefore, sample storage time or sample recovery studies to determine or verify inertness of the sampling canister should be considered.

Canisters are generally used to collect samples by slowly opening the sample valve, allowing the vacuum to draw in the sample gas. In less than a minute, the container should equilibrate with the ambient atmospheric pressure. At that time, the sample valve is closed to retain the sample. To collect composite samples over longer intervals, small calibrated orifices can be inserted before the inlet valve to extend the time required for equilibration of pressure once the sample valve is opened.

The sample collection procedure for EPA Method 5 (U.S. EPA, 1981) is similar in principle to that for the evacuated canister. The train consists of a polished stainless steel canister with a cold condensate trap in series and prior to the canister to collect a higher boiling point organic fraction. This two fraction apparatus provides for separate collection of two concentration ranges of volatile organic compounds based on boiling point.

The following four sampling methods utilize sample concentration techniques using one or more sorbent traps. The advantages of these methods is an enhanced limit of detection for many toxic and hazardous organic compounds. These techniques are preferred due to their lower detection limit. The Modified Method 5 (MM5) sampling train (U.S. EPA, 1981) is used to sample gaseous effluents for vapor-phase organic compounds that exhibit vapor pressures of less than 2 mm Hg (at 20°C). This system is a modification of the conventional EPA Method 5 particulate sampling train. The modified system consists of a probe, a high efficiency glass or

quartz fiber filter, a sorbent module, impingers, and related control hardware. The sample gas is passed through a single sorbent trap, containing XAD-2. The MM5 train is limited due to the single sorbent trap design that does not provide a backup for breakthrough. This is especially important when large volumes of sample are collected.

To minimize the potential for breakthrough, the MM5 train can be modified to provide a backup trap. However, this dual trap modification increases the pressure drop across the train, reducing the range of flow rates possible for sample collection. To overcome this pressure drop and maintain the desired flow rate, the high-volume MM5 train utilizes a much larger capacity pump.

The Source Assessment Sampling System (SASS) train is another comprehensive sampling train, consisting of a probe that connects to three cyclones and a filter in a heated oven module, a gas treatment section, and a series of impingers to provide large collection capacities for particulate matter, semivolatiles, and other lower volatility organics. The materials of construction are all stainless steel making the system very heavy and cumbersome. The stainless steel construction is also very susceptible to corrosion. This system can, however, be used to collect and concentrate large sample volumes, providing for a much lower detection limit. Because of the sorbents used (generally XAD-2), its use is limited to the same class of lower volatility organics and metals as the MM5 train.

The Volatile Organic Sampling Train (VOST) has proven to be a reliable and accurate method for collection of the broad range of organic compounds. By using a dual sorbent and dual in-series trap design, the VOST train can supplement either the MM5 or SASS methods allowing for collection of more volatile species. However, VOST has several limitations, including a maximum sample flow rate of 1.0 liter/minute, and a total sample volume of 20 liters per trap pair. Therefore, frequent changes of the trap pairs are required for test periods that exceed 20 minutes. The frequent change of traps makes the samples more susceptible to contamination.

Any of the point source monitoring techniques described above can be adapted for use with the isolation flux chamber techniques described previously. For point sources where particulate emissions are of concern, the Modified Method

5 or SASS train (originally designed to measure particle emissions from combustion effluents) are also applicable and proven technologies.

Analytical methodologies for the techniques discussed above will vary with the technique used. While certain techniques will offer advantages over others in the measurement of specific contaminants, the investigator is advised to utilize standard methodologies whenever possible in performing the RFI. For example, use of the VOST and/or the MM5 train, and their associated analytical methodologies is recommended for point source monitoring of the applicable compounds. Descriptions for both of these methods are included in the 3rd Edition of "Test Methods for Evaluating Solid Waste" (EPA SW-846), 1986 (GPO No. 955-001-00000-1). Although these methods are designed for the evaluation of incinerator efficiencies, they are essentially point-source monitoring methods which can be adapted to most point sources.

12.8.3.2 Metals

Although the emission of metallic contaminants is primarily associated with particulate emission from area sources caused by the transfer of material to and from different locations, wind erosion, or general maintenance and traffic activities at the unit, point source emission of particulate or vapor-phase metals can exist. Metallic constituents may exist in the atmosphere as solid particulate matter, as dissolved or suspended constituents of liquid droplets (mists), and as vapors.

Metals specified as hazardous constituents in 40 CFR Part 261, Appendix VIII are generally noted as the element and compounds "not otherwise specified (NOS)", as shown in Table 12-21, indicating that measurement of the total content of that element in the sample is required.

Vapor phase metals--For the purpose of point-source monitoring, vapor-phase metals will be defined as all elements or compounds thereof, that are not quantitatively captured by standard filter sampling procedures. These include volatile forms of metals such as elemental and alkyl mercury, arsine, antimony, alkyl lead compounds, and nickel carybonyl.

Table 12-21.

RCRA APPENDIX VIII HAZARDOUS METALS AND METAL COMPOUNDS

Antimony and compounds NOS[a]
Arsenic and compounds NOS[b]
Barium and compounds NOS[b]
Beryllium and compounds NOS
Cadmium and compounds NOS
Chromium and compounds NOS
Lead and compounds NOS
Mercury and compounds NOS[b]
Nickel and compounds NOS[b]
Selenium and compounds NOS[b]
Silver and compounds NOS[b]
Thallium and compounds NOS[b]

[a] NOS = not otherwise specified.

[b] Additional specific compound(s) listed for this element.

The sampling of point sources for vapor phase metals has not been a common or frequent activity for the investigation of air releases from solid waste management units. If a point source of vapor-phase metals is identified, the sampling approach should identify the best available monitoring techniques, considering that many have been developed which are specific to single species rather than multiple species of many different metal elements. The primary references for identifying available techniques include National Institute of Occupational Safety and Health (NIOSH, 1984) methods, EPA methods such as those presented in SW-846 and in the Federal Register under the National Emissions Standards for Hazardous Air Pollutants (NESHAPs), and American Public Health Association (APHA, 1977) methods. The basic monitoring techniques include collection on sorbents and in impinger solutions. The particular sorbent or impinger solution utilized should be selected based on the specific metal species under investigation.

Particulate Metals--Point-source releases to air could also require investigation of particulate metals. Source sampling particulate procedures such as the Modified Method 5 or SASS methods previously discussed are appropriate for this activity. EPA Modified Method 5 is the recommended approach. Modification of this basic technique involving the collection of particulate material on a filter with subsequent analysis of the collected particulate materal on a filter for the metals of concern, could include higher or lower flow rates and the use of alternate filter media. Such modificaitons may be proposed when standard techniques prove to be inadequate. Several important particulate metal sampling methods are available in the NIOSH methods manuals (NIOSH, 1984); however, these methods were designed for ambient or indoor applications and may require modification if used on point sources.

12.9 Site Remediation

Although the RFI Guidance is not intended to provide detailed guidance on site remediation, it should be recognized that certain data collection activities that may be necessary for a Corrective Measures Study may be collected during the RFI. EPA has developed a practical guide for assessing and remediating contaminated sites that directs users toward technical support, potential data requirements and

technologies that may be applicable to EPA programs such as RCRA and CERCLA. The reference for this guide is provided below.

U.S. EPA. 1988. Practical Guide for Assessing and Remediating Contaminated Sites. Office of Solid Waste and Emergency Response. Washington, D.C. 20460.

The guide is designed to address releases to ground water as well as soil, surface water and air. A short description of the guide is provided in Section 1.2 (Overall RCRA Corrective Action Process), under the discussion of Corrective Measures Study.

12.10 Checklist

RFI CHECKLIST - AIR

Site Name/Location _____

Type of Unit _____

1. Does waste characterization include the following information? (Y/N)

   - Physical form of the waste _____
   - Identification of waste components _____
   - Concentrations of constituents of concern _____
   - Chemical and physical properties of constituents of concern _____

2. Does unit characterization include the following information? (Y/N)

   - Type of unit _____
   - Types and efficiencies of control devices _____
   - Operational schedules _____
   - Operating logs _____
   - Dimensions of the unit _____
   - Quantities of waste managed _____
   - Locations and spatial distribution/ variation of waste in the unit _____
   - Past odor complaints from neighbors _____
   - Existing air monitoring data _____
   - Flow rates from vents _____

3. Does environmental setting characterization include the following information? (Y/N)

   - Definition of regional climate _____
   - Definiation of site-specific meteorological conditions _____
   - Definition of soil conditions _____

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- Definition of site-specific terrain _____
- Identification of potential release receptors _____

4. Have the following data on the initial phase of the release characterization been collected? (Y/N)

   - Conceptual model of release developed _____
   - Concentrations of released constituent at unit, facility property boundary and, if appropriate, at nearby offsite receptors (based on screening assessment or available modeling/monitoring data) _____
   - Screening monitoring data (as warranted) _____
   - Additional waste/unit data (as warranted) _____

5. Have the following data on the subsequent phase(s) of the release characterization been collected? (Y/N)

   - Identification of "reasonable worst case" conditions _____
   - Meteorological conditions during monitoring _____
   - Release source conditions during monitoring _____
   - Basis for selection of monitoring constituents _____
   - Concentrations of released constituents at unit, facility property boundary and, if appropriate, at nearby offsite receptors (based on monitoring or modeling and representative of reasonable "worst case" conditions) _____

12.11 References

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SECTION 13

SURFACE WATER

13.1 Overview

The objective of an investigation of a release to surface water is to characterize the nature, extent, and rate of migration of the release to this medium. This section provides the following:

- An example strategy for characterizing releases to the surface water system (e.g., water column, bottom sediments, and biota), which includes characterization of the source and the environmental setting of the release, and conducting a monitoring program that will characterize the release;

- A discussion of waste and unit source characteristics and operative release mechanisms;

- A strategy for the design and conduct of monitoring programs considering specific requirements of different wastes, release characteristics, and receiving water bodies;

- Formats for data organization and presentation;

- Appropriate field and other methods that may be used in the investigation; and

- A checklist of information that may be needed for release characterization.

The exact type and amount of information required for sufficient release characterization will be facility and site-specific and should be determined through interactions between the regulatory agency and the facility owner or operator during the RFI process. This guidance does not define the specific data needed in all

instances; however, it identifies the information that is likely to be needed to perform release characterizations and identifies methods for obtaining this information. The RFI Checklist, presented at the end of this section, provides a tool for planning and tracking information collection for release characterization. This list is not a list of requirements for all releases to surface water. Some releases will involve the collection of only a subset of the items listed, while others will involve the collection of additional data.

Case Study Numbers 27, 28, 29, 30 and 31 in Volume IV (Case Study Examples) illustrate various aspects of surface water investigations which are described below.

13.2 Approach for Characterizing Releases to Surface Water

13.2.1 General Approach

A conceptual model of the release should be formulated using all available information on the waste, unit characteristics, environmental setting, and any existing monitoring data. This model (not a computer or numerical simulation model) should provide a working hypothesis of the release mechanism, transport pathway/mechanism, and exposure route (if any). The model should be testable/verifiable and flexible enough to be modified as new data become available. For surface water investigations, this model should account for the release mechanism (e.g., overtopping of an impoundment), the nature of the source area (e.g., point or non-point), waste type and degradability, climatic factors (e.g., history of floods), hydrologic factors (e.g., stream flow conditions), and fate and transport factors (e.g., ability for a contaminant to accumulate in stream bottom sediments). The conceptual model should also address the potential for the transfer of contaminants in surface water to other environmental media (e.g., soil contamination as a result of flooding of a contaminated creek on the facility property).

An example strategy for characterization of releases to surface waters is summarized in Table 13-1. These steps outline a phased approach, beginning with evaluation of existing data and proceeding to design and implementation of a monitoring program, revised over time, as necessary, based on findings of the previous phase. Each of these steps is discussed briefly below.

TABLE 13-1

EXAMPLE STRATEGY FOR CHARACTERIZING RELEASES TO SURFACE WATER*

INITIAL PHASE

1. Collect and review existing information on:

   - Waste
   - Unit
   - Environmental setting
   - Contaminant releases, including inter-media transport

2. Identify any additional information necessary to fully characterize release:

   - Waste
   - Unit
   - Environmental setting
   - Contaminant releases, including inter-media transport

3. Develop monitoring procedures:

   - Formulate conceptual model of release
   - Determine monitoring program objectives
   - Select monitoring constituents and indicator parameters
   - Select monitoring locations
   - Determine monitoring frequency
   - Incorporate hydrologic monitoring as necessary
   - Determine role of biomonitoring and sediment monitoring

4. Conduct initial monitoring:

   - Collect samples under initial monitoring phase procedures and complete field analyses
   - Analyze samples for selected parameters and constituents

5. Collect, evaluate, and report results:

   - Compare analytical and other monitoring procedure results to health and environmental criteria and identify and respond to emergency situations and identify priority situations that may warrant interim corrective measures - Notify regulatory agency
   - Summarize and present data in appropriate format
   - Determine if monitoring program objectives were met
   - Determine if monitoring locations, constituents and frequency were adequate to characterize release (nature, extent, and rate)
   - Report results to regulatory agency

TABLE 13-1 (continued)

EXAMPLE STRATEGY FOR CHARACTERIZING RELEASES TO SURFACE WATER*

SUBSEQUENT PHASES (If necessary)

1. Identify additional information necessary to characterize release:

   - Identify additional information needs
   - Determine need to include or expand hydrologic, and sediment and bio-monitoring
   - Evaluate potential role of inter-media transport

2. Expand initial monitoring as necessary:

   - Relocate, decrease, or increase number of monitoring locations
   - Add or delete constituents and parameters of concern
   - Increase or decrease monitoring frequency
   - Delete, expand, or include hydrologic, sediment or bio-monitoring

3. Conduct subsequent monitoring phases:

   - Collect samples under revised monitoring procedures and complete field analyses
   - Analyze samples for selected parameters and constituents

4. Collect, evaluate and report results/identify additional information necessary to characterize release:

   - Compare analytical and other monitoring procedure results to health and environmental criteria and identify and respond to emergency situations and identify priority situations that may warrant interim corrective measures - Notify regulatory agency
   - Determine if monitoring program objectives were met
   - Determine if monitoring locations, constituents, and frequency were adequate to characterize release (nature, extent, and rate)
   - Identify additional information needs
   - Determine need to include or expand hydrologic, sediment, or bio-monitoring
   - Evaluate potential role of inter-media transport
   - Report results to regulatory agency

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* Surface water system is subject to inter-media transport. Monitoring program should incorporate the necessary procedures to characterize the relationship, if any, with ground water, sediment deposition, fugitive dust and other potential release migration pathways.

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The first step in the general approach is the collection and review of available information on the contaminant source and the environmental setting. Some information on the contaminant source will be available from several reports and other documents. The RCRA permit, compliance order, or RFA report will provide a summary of information regarding actual or suspected releases from the various units. The facility owner or operator should be familiar with this information as a basis for further characterization of the release(s) in the RFI. In addition, a thorough understanding of the environmental setting is essential to an adequate determination of the nature and extent of releases to surface waters. Monitoring data should also be reviewed focusing on the quality of the data. If the quality is determined to be acceptable, then the data may be used in the design of the monitoring program. Guidance on obtaining and evaluating the necessary information on the contaminant source and the environmental setting is given in Section 13.3.

During the initial investigation particular attention should be given to sampling run-off from contaminated areas, leachate seeps and other similar sources of surface water contamination, as these are the primary overland release pathways for surface water. Releases to surface water via ground-water discharge should be addressed as part of the ground-water investigation, which should be coordinated with surface water investigations, for greater efficiency.

Based on the collection and review of existing information, the design of the monitoring program is the next major step in the general approach. The monitoring program should include clear objectives, monitoring constituents and indicator parameters, monitoring locations, frequency of monitoring, and provisions for hydrologic monitoring. In addition to conventional water quality and hydrologic monitoring, sediment monitoring and biomonitoring may also have a role in the surface water evaluation for a given RFI. Guidance on the design of the monitoring program is given in Section 13.4.

Implementation of the monitoring program is the next major step in the general strategy for characterizing releases to surface water. The program may be implemented in a phased manner that allows for modifications to the program in subsequent phases. For example, initial monitoring results may indicate that

downstream monitoring locations have been placed either too close to or too far from the contaminant source to accurately define the complete extent of downstream contamination. In this case, the program should be modified to relocate monitoring stations for subsequent monitoring phases. Similarly, initial monitoring may indicate that biomonitoring of aquatic organisms is needed in the next phase. Guidance on methods that can be used in the implementation of the program is given in Section 13.6.

Finally, the results of the characterization of releases to surface waters must be evaluated and presented in conformance with the requirements of the RFI. Section 13.5 provides guidance on data presentation. Table 13-2 summarizes techniques and data-presentation methods for the key characterization tasks.

As monitoring data become available, both within and at the conclusion of discrete investigation phases, they should be reported to the regulatory agency as directed. The regulatory agency will compare the monitoring data to applicable health and environmental criteria to determine the need for (1) interim corrective measures; and/or (2) a Corrective Measures Study. In addition, the regulatory agency will evaluate the monitoring data with respect to adequacy and completeness to determine the need for any additional monitoring efforts. The health and environmental criteria and a general discussion of how the regulatory agency will apply them are supplied in Section 8. A flow diagram illustrating RFI decision points is provided in Section 3 (See Figure 3-2).

Notwithstanding the above process, the owner or operator has a continuing responsibility to identify and respond to emergency situations and to define priority situations that may warrant interim corrective measures. For these situations, the owner or operator is directed to follow the RCRA Contingency Plan requirements under 40 CFR Part 264, Subpart D and Part 265, Subpart D.

TABLE 13-2
RELEASE CHARACTERIZATION TASKS FOR SURFACE WATER

Investigatory Tasks	Investigatory Techniques	Data Presentation Formats/Outputs
1. Waste/Unit Characterization		
- Waste Composition and Analysis	- See Section 13.3.1	- Data Tables
- Unit or Facility Operations	- Review waste handling and disposal practices and schedules - Review environmental control strategies	- Schematic diagrams of flow paths, narrative
- Release Mechanisms	- See Section 13.3.1, Review operational information	- Site-specific diagrams, maps, narrative
2. Environmental Setting Characterization		
- Geographic Description	- Review topographic, soil and geologic setting information	- Maps, Tables, Narrative
- Classification of Surface Water and Receptors	- See Section 13.3.3.1	- Maps, Cross Sections, Narrative
- Define Hydrologic Factors	- See Section 13.3.3.1	- Tables, Graphs, Map
3. Release Characterization		
- Delineate Areal Extent of Contamination	- Sampling and Analysis	- Tables of Results, Contour Maps, Maps of Sampling Locations
- Define Distribution Between Sediment, Biota and Water Column	- Sampling and Analysis	- Graphs and Tables
- Determine Rate of Migration	- Flow Monitoring	- Graphs and Tables
- Describe Seasonal Effects	- Repetitive Monitoring	- Graphs and Tables

13.2.2 Inter-media Transport

Surface waters are subject to inter-media transport, both as a receptor of contamination and as a migration pathway. For example, surface waters are generally engaged in a continual dynamic relationship with ground water. Ground water may discharge to a surface water body that may, in turn, recharge an aquifer. Hence, contamination may be transported from ground water to surface water and from surface water to ground water. Release of contaminants from a receiving water body to soil can also occur through deposition of the contaminants in floodplain sediments. These sediments may be exposed to wind erosion and become distributed through fugitive dust. Sediments may be exposed to air during periods of low flow of water in streams and lakes and when sediments are deposited by overland flow during rainfall-runoff events. Contaminants may also enter the air from surface water through volatilization.

13.3 Characterization of the Contaminant Source and Environmental Setting

The initial step in developing an effective monitoring program for a release to surface waters is to investigate the unit(s) that is the subject of the RFI, the waste within the unit(s), the constituents within the waste, the operative release mechanisms and migration pathways to surface water bodies, and the surface water receptors. From this information, a conceptual model of the release can be developed for use in designing a monitoring program to characterize the release.

13.3.1 Waste Characterization

Knowledge of the general types of wastes involved is an important consideration in the development of an effective monitoring program. The chemical and physical properties of a waste and the waste constituents are major factors in determining the likelihood that a substance will be released. These waste properties may also be important initially in selecting monitoring constituents and indicator parameters. Furthermore, once the wastes are released, these properties play a major role in controlling the constituent's migration through the environment and its fate. Table 13-3 lists some of the significant properties in evaluating environmental fate and transport in a surface water system. Without data on the wastes, the investigator may have to implement a sampling program

TABLE13-3

IMPORTANT WASTE AND CONSTITUENT PROPERTIES AFFECTING FATE AND TRANSPORT IN A SURFACE WATER ENVIRONMENT

Bulk waste properties affecting mobility[a]

- Physical state (solid, liquid, gas) of waste
- Chemical nature (e.g., aqueous vs non-aqueous) of waste
- Density (liquid)
- Viscosity (liquid)
- Interfacial tension (with water and minerals) (liquid)

Properties to assess mobility of constituents[b]

- Solubility
- Vapor pressure
- Henry's law constant (or vapor pressure and water solubility)
- Bioconcentration factor
- Soil adsorption coefficient
- Diffusion coefficient (in air and water)
- Acid dissociation constant
- Octanol-water partition coefficient
- Activity coefficient
- Mass transfer coefficients (and/or rate constants) for intermedia transfer
- Boiling point
- Melting point

Properties to assess persistence[c]

- Rate of biodegradation (aerobic and anaerobic)
- Rate of hydrolysis
- Rate of oxidation or reduction
- Rate of photolysis

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a These waste properties will be important when it is known or suspected that the waste itself has migrated into the environment (e.g., due to a spill).

b These properties are important in assessing the mobility of constituents present in low concentrations in the environment.

c For these properties, it is generally important to know (1) the effects of key parameters on the rate constants (e.g., temperature, concentration, pH) and (2) the identity of the reaction products.

Sources of values for these and other parameters include Mabey, Smith, and Podall, (1982), and Callahan, et al. (1979). Parameter estimation methods are described by Lyman, Riehl, and Rosenblatt, (1982), and Neely and Blau (1985).

involving many constituents to ensure that all potential constituents have been addressed. General guidance on defining physical and chemical properties and identifying possible monitoring constituents and indicator parameters is provided in Sections 3 and 7.

Below are brief synopses of several of the key release, mobility, and fate parameters summarized in Table 13-3. Figure 13-1 shows the qualitative relationship between various environmental partitioning parameters. Neely and Blau (1985) provide a description of environmental partitioning effects of constituents and application of partition coefficients.

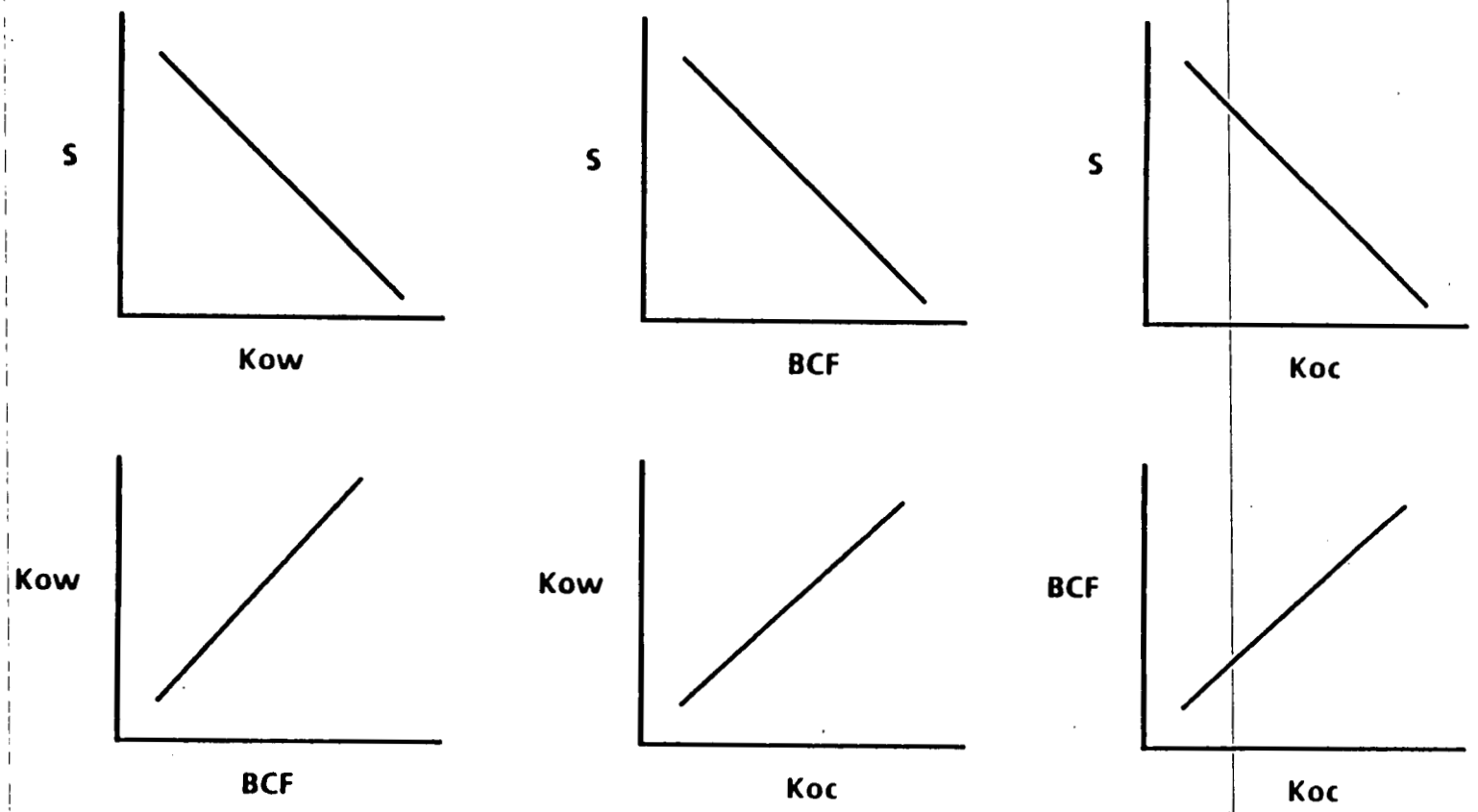
- Physical State:
  Solid wastes would appear to be less susceptible to release and migration than liquids. However, processes such as dissolution (i.e., as a result of leaching or runoff), and physical transport of waste particulates can act as significant release mechanisms.

- Water Solubility:
  Solubility is an important factor affecting a constituent's release and subsequent migration and fate in the surface water environment. Highly soluble contaminants (e.g., methanol at 4.4×10^6 mg/L at 77°F) are easily and quickly distributed within the hydrologic cycle. These contaminants tend to have relatively low adsorption coefficients for soils and sediments and relatively low bioconcentration factors in aquatic life. An example of a less soluble constituent is tetrachloroethylene at 100 mg/L at 77°F.

- Henry's Law Constant:
  Henry's Law Constant indicates the relative tendency of a constituent to volatilize from aqueous solution to the atmosphere based on the competition between its vapor pressure and water solubility. Contaminants with low Henry's Law Constant values (e.g., methanol, 1.10×10^{-6} atm-m^3/mole at 77°F) will tend to favor the aqueous phase

FIGURE 13-1

QUALITATIVE RELATIONSHIP BETWEEN VARIOUS PARTITIONING PARAMETERS



S: Solubility

Kow: Octanol/water partition coefficient

BCF: Bioconcentration factor

Koc: Soil/sediment adsorption coefficient

and volatilize to the atmosphere more slowly than constituents with high values (e.g., carbon tetrachloride, 2.3 x 10^{-2} atm-m^3/mole at 77°F). This parameter is important in determining the potential for inter-media transport to the air media.

- Octanol/Water Partition Coefficient (K_{ow}):
  The octanol/water partition coefficient (K_{ow}) is defined as the ratio of an organic constituent's concentration in the octanol phase (organic) to its concentration in the aqueous phase in a two-phase octanol/water system. Values of K_{ow} carry no units. K_{ow} can be used to predict the magnitude of an organic constituent's tendency to partition between the aqueous and organic phases of a two phase system such as surface water and aquatic organisms. The higher the value of K_{ow}, the greater the tendency of an organic constituent to adsorb to soil or waste matrices containing appreciable organic carbon or to accumulate in biota. Generally, constituents with K_{ow} values greater than or equal to 2.3 are considered potentially bioaccumulative (Veith, et al., 1980).

- Soil-Water Partition Coefficient (K_d):
  The mobility of contaminants in soil depends not only on properties related to the physical structure of the soil, but also on the extent to which the soil material will retain, or adsorb, the hazardous constituents. The extent to which a constituent is adsorbed depends on chemical properties of the constituent and of the soil. Therefore, the sorptive capacity must be determined with reference to a particular constituent and soil pair. The soil-water partition coefficient (K_d) is generally used to quantify soil sorption. K_d is the ratio of the adsorbed contaminant concentration to the dissolved concentration, at equilibrium.

- Bioconcentration Factor (BCF):
  The bioconcentration factor is the ratio of the concentration of the constituent in an organism or whole body (e.g., a fish) or specific tissue (e.g., fat) to the concentration in water. Ranges of BCFs for various constituents and organisms are reported in the literature (Callahan, et al., 1979) and these values can be used to predict the potential for

bioaccumulation, and therefore to determine whether sampling of the biota may be necessary. Another source of BCFs for constituents is contained in EPA's Ambient Water Quality Criteria (for priority pollutants). BCFs can also be predicted by structure-activity relationships. Constituents exhibiting a BCF greater than 1.0 are potentially bioaccumulative. Generally, constituents exhibiting a BCF greater than 100 cause the greatest concern.

- The Organic Carbon Adsorption Coefficient (K_{oc}):
  The extent to which an organic constituent partitions between the solid and solution phases of a saturated or unsaturated soil, or between runoff water and sediment, is determined by the physical and chemical properties of both the constituent and the soil (or sediment). The tendency of a constituent to be adsorbed to soil is dependent on its properties and on the organic carbon content of the soil or sediment. K_{oc} is the ratio of the amount of constituent adsorbed per unit weight of organic carbon in the soil or sediment to the concentration of the constituent in aqueous solution at equilibrium. K_{oc} can be used to determine the partitioning of a constituent between the water column and the sediment. When constituents have a high K_{oc}, they have a tendency to partition to the soil or sediment. In such cases, sediment sampling would be appropriate.

- Other Equilibrium Constants:
  Equilibrium constants are important predictors of a compound's chemical state in solution. In general, a constituent which is dissociated (ionized) in solution will be more soluble and therefore more likely to be released to the environment and more likely to migrate in a surface water body. Many inorganic constituents, such as heavy metals and mineral acids, can occur as different ionized species depending on pH. Organic acids, such as the phenolic compounds, exhibit similar behavior. It should also be noted that ionic metallic species present in the release may have a tendency to bind to particulate matter, if present in a surface water body, and settle out to the sediment over time and distance. Metallic species also generally exhibit bioaccumulative properties. When metallic

species are present in a release, both sediment and biota sampling would be appropriate.

- Biodegradation:
  Biodegradation results from the enzyme-catalyzed transformation of organic constituents, primarily from microorganisms. The ultimate fate of a constituent introduced into a surface water or other environmental system (e.g., soil), could be a constituent or compound other than the species originally released. Biodegradation potential should therefore be considered in designing monitoring programs. Section 9.3 (Soils) presents additional information on biodegradation.

- Photolysis:
  Photodegradation or photolysis of constituents dissolved in aquatic systems can also occur. Similar to biodegradation, photolysis may cause the ultimate fate of a constituent introduced into a surface water or other environmental system (e.g., soil) to be different from the constituent originally released. Hence, photodegradation potential should also be considered in designing sampling and analysis programs.

- Chemical Degradation (Hydrolysis and Oxidation/Reduction):
  Similar to photodegradation and biodegradation, chemical degradation, primarily through hydrolysis and oxidation/reduction (REDOX) reactions, can also act to change constituent species once they are introduced to the environment. Hydrolysis of organic compounds usually results in the introduction of a hydroxyl group (-OH) into a chemical structure. Hydrated metal ions, particularly those with a valence of 3 or more, tend to form ions in aqueous solution, thereby enhancing species solubility. Mabey and Mill (1978) provide a critical review of the hydrolysis of organic compounds in water under environmental conditions. Stumm and Morgan (1982) discuss the hydrolysis of metals in aqueous systems. Oxidation may occur as a result of oxidants being formed during photochemical processes in natural waters. Similarly, in some surface water environments (primarily those with low oxygen levels) reduction of constituents may take place.

Degradation, whether biological, physical or chemical, is often reported in the literature as a half-life, which is usually measured in days. It is usually expressed as the time it takes for one half of a given quantity of a compound to be degraded. Long half-lives (e.g., greater than a month or a year) are characteristic of persistent constituents. It should be noted that actual half-life can vary significantly over reported values based on site-specific conditions. For example, the absence of certain microorganisms at a site, or the number of microorganisms, can influence the rate of biodegradation, and therefore, half-life. Other conditions (e.g., temperature) may also affect degradation and change the half-life. As such, half-life values should be used only as general indications of a chemical's persistence.

In addition to the above, reactions between constituents present in a release may also occur. The owner or operator should be aware of potential transformation processes, based on the constituents' physical, chemical and biological properties, and account for such transformations in the design of monitoring procedures and in the selection of analytical methods.

Table 13-4 provides an application of the concepts discussed above in assessing the behavior of waste material with respect to release, migration, and fate. The table gives general qualitative descriptors of the significance of some of the more important properties and environmental processes for the major classes of organic compounds likely to be encountered.

Table 13-4 can be used to illustrate several important relationships.

- Generally, water solubility varies inversely with sorption, bioconcentration, and to a lesser extent, volatilization.

- Oxidation is a significant fate process for some classes of constituents which can volatilize from the aqueous phase.

- Variations in properties and environmental processes occur within classes as indicated by the pesticides, monocyclic aromatics, polycyclic aromatics, and the nitrosamines and other nitrogen-containing compounds.

TABLE 13-4

GENERAL SIGNIFICANCE OF PROPERTIES AND ENVIRONMENTAL PROCESSES FOR CLASSES OF ORGANIC CHEMICALS UNDER ENVIRONMENTAL CONDITIONS

Chemical Class	Solubility	Sorption	Bioconcentration	Volatilization	Photolysis	Oxidation	Hydrolysis
Pesticides							
Organochlorines	Low	High	High	High	Moderate	Low	Low
Organophosphates	Moderate	Moderate	Low	Low	High	High	Moderate-High
Carbamates	Moderate	Moderate	Moderate	Low	Moderate	Moderate	Moderate
Polychlorinated Biphenyls	Low	High	High	Moderate	Low	Low	Low
Halogenated Aliphatics	Moderate	Low	Low	High	Low	High*	Low
Halogenated Ethers	High	Low	Low	Low	Low	High*	High
Monocyclic Aromatics							
Toluene	Moderate	Moderate	Low	High	Low	High*	Low
Phenol	High	Low	Low	Low-Moderate	Moderate	Moderate	Low
Phthalate Esters	Low	High	High	Low	Low	Low	Low
Polycyclic Aromatics							
Naphthalene	Moderate	High	Low	Moderate	High**	Low	Low
Benzo(K)Fluoranthene	Low	High	Low	Low	High**	Low	Low
Nitrosamines and other Nitrogen-Containing Compounds							
Benzedine	Moderate-High	High	Low	Low	High	High	Low
Di-n-propylnitrosamine	High	Low	Low	Low	High	Low	Low

* Atmospheric oxidation (volatile organic chemicals).

** Dissolved portion only.

Table entries are qualitative only and based on a typical chemical within the class. Variations are observed within each class.

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Characterizing the environmental processes and properties of inorganic waste constituents takes a similar approach to that shown on Table 13-4 for organics. However, characterizing the metals on a class-by-class basis is not advisable because of the complex nature of each metal and the many species in which the metals generally occur. The interaction of each metal species with the surface water environment is generally a function of many parameters including pH, REDOX potential, and ionic strength. See Stumm and Morgan (1982) for additional discussions on this subject. Generally, however, when metal species are present in a release, it is advisable to monitor the sediment and biota, in addition to the water column. This is due to likely deposition of metals as particulate matter, and to potential bioaccumulation.

13.3.2 Unit Characterization

The relationship between unit characteristics and migration pathways provides the framework in this section for a general discussion of release mechanisms from units of concern to surface waters.

13.3.2.1 Unit Characteristics

Information on design and operating characteristics of a unit can be helpful in characterizing a release. Unsound unit design and operating practices can allow waste to migrate from a unit and possibly mix with runoff. Examples include surface impoundments with insufficient freeboard, allowing for periodic overtopping; leaking tanks or containers; or land-based units above shallow, low-permeability materials which, if not properly designed and operated, can fill with water and spill over. In addition, precipitation falling on exposed wastes can dissolve and thereby mobilize hazardous constituents. For example, at uncapped active or inactive waste piles and landfills, precipitation and leachate are likely to mix at the toe of the active face or the low point of the trench floor. Runoff may then flow into surface water through drainage pathways.

13.3.2.2 Frequency of Release

Releases to surface waters may be intermittent, continuous, or a past occurrence. It is important to consider the anticipated frequency of a release to establish an effective monitoring program.

Most direct releases to surface waters are intermittent. Intermittent discharges may be periodic, but may occur more often in a non-periodic manner, for example, in response to rainfall runoff. Other common factors affecting intermittent releases include fluctuations in water levels and flow rates, seasonal conditions (e.g., snow melt), factors affecting mass stability (e.g., waste pile mass migration), basin configuration, quantity/quality of vegetation, engineering control practices, integrity of the unit, and process activities.

Erosion of contaminated materials from a unit (e.g., a landfill) is generally intermittent, and is generally associated with rainfall-runoff events. Similarly, breaches in a dike are generally short-term occurrences when they are quickly corrected following discovery. Leaks, while still predominantly intermittent in nature, may occur over longer spans of time and are dependent on the rate of release and the quantity of material available.

Direct placement of wastes within surface waters (e.g., due to movement of an unstable waste pile) has the potential to continuously contribute waste constituents until the wastes have been removed or the waste constituents exhausted. Direct placement is usually easily documented by physical presence of wastes within the surface water body.

The frequency of sample collection should be considered in the design of the monitoring program. For example, intermittent releases not associated with precipitation runoff may require more frequent or even continuous sample collection to obtain representative data on the receiving water body. Continuous monitoring is generally feasible only for the limited number of constituents and indicator parameters for which reliable automatic sampling/recording equipment is available. Intermittent releases that are associated with precipitation runoff may require event sample collection. With event sampling, water level or flow-activated automatic sampling/recording equipment can be used. For continuous releases, less

frequent sample collection is generally adequate to obtain representative data on the receiving water body.

Previous intermittent releases may be identified through the analysis of bottom sediments, and whole body or tissue analyses of relatively sessile and long-lived macroinvertebrates (e.g., clams), or other species, such as fish. These analyses may identify constituents that may have adsorbed onto particulates and settled to the sediment, as well as bioaccumulative contaminants. In addition, intermittent releases may be detected through the use of in situ bioassays. Using these procedures, the test specie(s) is held within the effluent or stream flow and periodically checked for survival and condition.

13.3.2.3 Form of Release

Releases to surface waters may be generally categorized as point sources or non-point sources. Point sources are those that enter the receiving water at a definable location, such as piped discharges. Non-point source discharges are all other discharges, and generally cover large areas.

In general, most unit releases to surface waters are likely to be of a point source nature. Most spills, leaks, seeps, overtopping episodes, and breaches occur within an area which can be easily defined. Even erosion of contaminated soil and subsequent deposition to surface water can usually be identified in terms of point of introduction to the surface water body, through the use of information on drainage patterns, for example. However, the potential for both point and non-point sources should be recognized, as monitoring programs designed to characterize these types of releases can be different. For example, the generally larger and sometimes unknown areal extent of non-point source discharges may require an increase in the number of monitoring locations from that routinely required for point source discharges. The number of monitoring locations must be carefully chosen to ensure representative monitoring results.

13.3.3 Characterization of the Environmental Setting

The environmental setting includes the surface water bodies and the physical and biological environment. This section provides a general classification scheme for surface waters and discusses collection of hydrologic data that may be important in their characterization. Collection of specific geographical and climatological

data are also discussed. Characterization of the biotic environment is treated in Section 13.4.

Note that individual states have developed water quality standards for surface waters pursuant to the Clean Water Act. These standards identify the designated uses (e.g., drinking, recreation, etc.) of a surface water and a maximum contaminant level to support the use. If applicable, the owner or operator should report such standards.

13.3.3.1 Characterization of Surface Waters

Surface waters can be classified into one of the following categories. These are obviously not pure classifications; intergrades are common.

- Streams and rivers;
- Lakes and impoundments;
- Wetlands; and
- Marine environments.

13.3.3.1.1 Streams and Rivers

Streams and rivers are conduits of surface water flow having defined beds and banks. The physical characteristics of streams and rivers greatly influence their reaction to contaminant releases and natural purification (i.e., assimilative capacity). An understanding of the nature of these influences is important to effective planning and execution of a monitoring program. Important characteristics include depth, velocity, turbulence, slope, changes in direction and in cross sections, and the nature of the bottom.

The effects of some of these factors are so interrelated that it is difficult to assign greater or lesser importance to them. For example, slope and roughness of the channel influence depth and velocity of flow, which together control turbulence. Turbulence, in turn, affects rates of contaminant dispersion,

reaeration, sedimentation, and rates of natural purification. The nature of contaminant dispersion is especially critical in the location of monitoring stations. All these factors may be of greater or lesser importance for specific sites. It should also be noted that these factors may differ at the same site depending on when the release occurred. For example, differences between winter and summer flow may greatly influence the nature of contaminant dispersion.

Of further relevance to a surface water investigation are the distinctions between ephemeral, intermittent, and perennial streams, defined as follows:

- Ephemeral streams are those that flow only in response to precipitation in the immediate watershed or in response to snow melt. The channel bottom of an ephemeral stream is always above the local water table.

- Intermittent streams are those that usually drain watersheds of at least one square mile and/or receive some of their flow from baseflow recharge from ground water during at least part of the year, but do not flow continually.

- Perennial streams flow throughout the year in response to ground water discharge and/or surface water runoff.

The distinction between ephemeral, intermittent and perennial streams will also influence the selection of monitoring frequency, monitoring locations and possibly other monitoring program design factors. For example, the frequency of monitoring for ephemeral streams, and to a lesser extent intermittent streams, will depend on rainfall runoff. For perennial-stream monitoring, the role of rainfall runoff in monitoring frequency may be of less importance under similar release situations.

The location of ephemeral and intermittent streams may not be apparent to the owner or operator during periods of little or no precipitation. Generally, intermittent and ephemeral streams may be associated with topographic depressions in which surface water runoff is conveyed to receiving waters. In addition to topography, a high density of vegetation in such areas may be an indicator of the presence of ephemeral or intermittent drainage.

Perennial streams and rivers are continually engaged in a dynamic relationship with ground water, either receiving ground-water discharge (gaining stream) or recharging the ground water (losing stream) over any given stream reach. These characteristics should be considered in the evaluation of contaminant transport and fate.

The Ecology of Running Waters (Hynes 1970) and Introduction to Hydrology (Viessman et al., 1977) may be reviewed for basic discussions of surface water hydrology.

13.3.3.1.2 Lakes and Impoundments

Lakes are typically considered natural, while impoundments may be man-made. The source for lakes and impoundments may be either surface water or ground water, or both. Impoundments may be either incised into the ground surface or may be created via the placement of a dam or embankment. As with streams and rivers, the physical characteristics of lakes and impoundments influence the transport and fate of contaminant releases and therefore the design of the monitoring program. The physical characteristics that should be evaluated include dimensions (e.g., length, width, shoreline, and depth), temperature distribution, and flow pathways.

Especially in the case of larger lakes and impoundments, flow paths are not clearcut from inlet to outlet. Not only is the horizontal component of flow in question, but as depth of the water body increases in the open water zone, chemical and more commonly physical (i.e., temperature) phenomena create a vertical stratification or zonation. Figure 13-2 provides a typical lake cross section, showing the various zones of a stratified lake.

Because of stratification, deeper water bodies can be considered to be comprised of three lakes. The upper lake, or epilimnion, is characterized by good light penetration, higher levels of dissolved oxygen, greater overall mixing due to wave action, and elevated biological activity. The lower lake, or hypolimnion, is the opposite of the epilimnion. Lying between these is what has been termed the

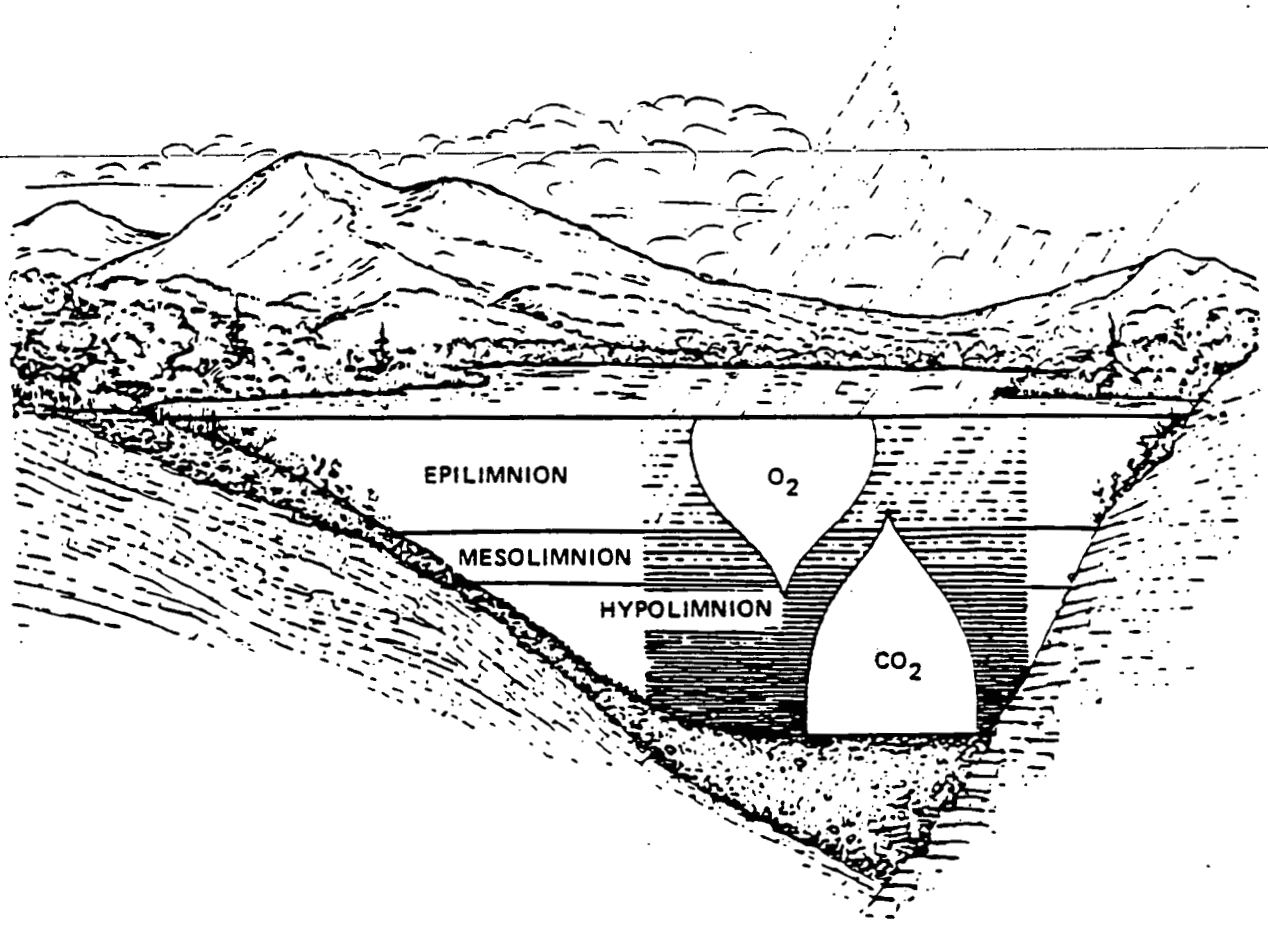

FIGURE 13-2. TYPICAL LAKE CROSS SECTION

(Source: Adapted from Cole, 1975).

middle lake or mesolimnion, characterized by a rapid decrease in temperature with depth. Were it not for the phenomenon of lake overturn, or mixing, contaminants with specific gravities greater than water might be confined to the lowermost lake strata, where they might remain for some time. Due to the potential importance of lake mixing to contaminant transport, it is discussed below.

Temperatures within the epilimnion are relatively uniform because of the mixing that occurs there. Water is most dense at 4° Centigrade (C); above and below 4°C its density decreases. In temperate climates, lake mixing is a seasonal occurrence. As the surface of the epilimnion cools rapidly in the fall, it becomes denser than the underlying strata. At some point, the underlying strata can no longer support the denser water and an "overturn" occurs, resulting in lake mixing. A similar phenomenon occurs in the spring as the surface waters warm to 4°C and once again become denser than the underlying waters.

Because of the influence of stratification on the transport of contaminants within a lake or reservoir, the location of monitoring points will largely depend on temperature stratification. The monitoring points on water bodies that are not stratified will be more strongly influenced by horizontal flowpaths, shoreline configuration and other factors. The presence of temperature stratification can be determined by establishing temperature-depth profiles of the water body.

More information on lakes and impoundments may be found in the following references:

A Treatise on Limnology, Volumes I and II (Hutchinson, 1957, 1967) or

Textbook of Limnology (Cole, 1975)

13.3.3.1.3 Wetlands

Wetlands are those areas that are inundated or saturated by surface or ground water at a frequency and duration sufficient to support, and that under normal circumstances do support, a prevalence of vegetation typically adapted for life in saturated soil conditions. Wetlands include, but are not limited to, swamps, marshes, bogs, and similar areas.

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Wetlands are generally recognized as one of the most productive and sensitive of biological habitats, often associated with critical habitat for State or Federally listed special-status species of plants or wildlife. Wetlands also may play a significant role in basin hydrology, moderating peak surface water flows and providing recharge to the ground water system. The definition of the extent and sensitivity of wetlands that may be affected by a release is essential to release characterization.

High organic content, fine-grained sediments, slow surface water movement and lush vegetative growth and biological activity contribute to a high potential for wetlands to concentrate contaminants from releases. This is especially true for bioaccumulative contaminants, such as heavy metals. The pH/Eh conditions encountered in many wetlands are relatively unique and can have a significant effect on a contaminant's toxicity, fate, etc. Seasonal die-off of the vegetation and flooding conditions within the basin may result in the wetlands serving as a significant secondary source of contaminants to downstream surface water receptors.

13.3.3.1.4 Marine Environments

For the purpose of this guidance, marine environments are restricted to estuaries, intermediate between freshwater and saline, and ocean environments. Industrial development near the mouths of rivers and near bays outletting directly into the ocean is relatively widespread, and the estuarine environment may be a common receptor of releases from industrial facilities.

Estuaries are influenced by both fresh water and the open ocean. They have been functionally defined as tidal habitats that are partially enclosed by land but have some access to the open sea, if only sporadically, and in which ocean water is partially diluted by fresh water. Estuaries may also experience conditions where salinities are temporarily driven above the ocean levels due to evaporative losses. Because of the protection afforded by encircling land areas, estuaries are termed "low-energy" environments, indicating that wave energy and associated erosive and mixing processes are reduced.

The physical characteristics of an estuary that will influence the design of a monitoring program are similar to those considered for lakes and impoundments (i.e., length, width, shoreline, depth, and flow pathways). However, the increased probability for chemical stratification due to varying salinities may be most pronounced in areas where freshwater streams and rivers discharge into the estuary. The monitoring program design should also consider tidal influences on stratification and contaminant dispersion.

In addition, estuaries, or some portions of estuaries, can be areas of intergrained sediment deposition. These sediments may contain a significant organic fraction, which enhances the opportunity for metal/organic adsorption, and subsequent bioaccumulation. Hence, biomonitoring within an estuary may also be appropriate. The ionic strength of contaminants may also have an important effect on their toxicity, fate, etc., in the marine environment.

13.3.3.2 Climatic and Geographic Conditions

A release to the surface water system will be influenced by local climatological/meteorological and geographic conditions. The release may be associated only with specific seasonal conditions like spring thaws or meteorological events such as storms. If the release is intermittent, the environmental conditions at the time of the release may help identify the cause of and evaluate the extent of the release. If the release is continuous, seasonal variations should also be evaluated.

The local climatic conditions should be reviewed to determine:

- The annual precipitation distribution (monthly averages);
- Monthly temperature variations;
- Diurnal temperature range (daytime/nighttime difference);
- Storm frequency and severity;
- Wind direction and speed; and

- Snowfall and snow pack ranges (if applicable).

This information will be useful in developing a sampling schedule and in selecting sampling methods. From these data, it should be possible to anticipate the range of climatic conditions at the site. These conditions may be far more complex than simple cold/hot or wet/dry seasons. Some areas have two or more "wet seasons", one characterized by prolonged showers, another by brief intense storms, and perhaps a third as a result of snowmelt. Cold/hot seasons may overlap these wet/dry seasons to create several climatologically identifiable seasons. Each season may affect the release differently and may require a separate characterization. The unique climatological seasons that influence the site should be identified. Typical winter, spring, summer and fall seasonal descriptions may not be appropriate or representative of the factors influencing the release. Sources of climatological data are given in Section 12 (Air).

In addition to the climatological/meteorological factors, local geographic conditions will influence the design of the sampling program. Topographic conditions and soil structure may make some areas prone to flash floods and stream velocities that are potentially damaging to sampling equipment. In other areas (e.g., the coastal dune areas of the southeastern states), virtually no runoff occurs. Soil porosity and vegetation are such that all precipitation either enters the ground water or is lost to evapotranspiration. (See Section 9 (Soil) for more information).

A description of the geographic setting will aid in developing a sampling program that is responsive to the particular conditions at the facility. When combined with a detailed understanding of the climatological/meteorological conditions in the area, a workable monitoring framework can be created.

13.3.4 Sources of Existing Information

Considerable information may already be available to assist in characterizing a release. Existing information should be reviewed to avoid duplication of previous efforts and to aid in focusing the RFI. Any information relating to releases from the unit, and to hydrogeological, meteorological, and environmental factors that could influence the persistence, transport or location of contaminants should be reviewed. This information may aid in:

- Delineating the boundaries of the sampling area;

- Choosing sampling and analytical techniques; and

- Identifying information needs for later phases of the investigation.

Information may be obtained from readily available sources of geological and meteorological data, waste characteristics, and facility operations records. (See also Sections 2, 3, 7 and Appendix A).

13.4 Design of a Monitoring Program to Characterize Releases

Following characterization of the contaminant source and environmental setting, a monitoring program is developed. This section outlines and describes factors that should be considered in design of an effective surface water monitoring program. The characterization of contaminant releases may take place in multiple phases. While the factors discussed in this section should be carefully considered in program design, each of these generic approaches may require modification for specific situations.

The primary considerations in designing a surface water monitoring program are:

- Establishing the objectives of the monitoring program;

- Determining the constituents of concern;

- Establishing the hydrologic characteristics of the receiving water and characteristics of the sediment and biota, if appropriate;

- Selecting constituents and/or indicators for monitoring;

- Selecting monitoring locations and monitoring frequency; and

- Determining the need for sediment monitoring and, hydrologic and biomonitoring.

13.4.1 Objectives of the Monitoring Program

The principal objectives of a monitoring program are to:

- Identify the characteristics of releases (e.g., continuous vs intermittent);
- Identify the fate of constituents;
- Identify the nature, rate, and extent of the release and actual or potential effects on water quality and biota; and
- Identify the effect of temporal variation on constituent fate and identify impacts on water quality and biota.

Periodic monitoring of the surface water system is often the only effective means of identifying the occurrence of releases and their specific effects. Releases can be continuous or intermittent, point source, or non-point source. The concept of monitoring is the same, regardless of the frequency or form of the release. A series of measurements, taken over time, better approximate the actual release to surface waters than a one-time grab sample.

The functional difference between monitoring the various types of discharges is the point of measurement. Point source discharges may be monitored at and/or near the discharge point to surface waters. The fate and potential effects of non-point source discharges should be inferred through measurement of the presence of constituents of concern or suitable indicators of water quality within the receiving water body.

The monitoring program should also establish the background condition against which to measure variations in a continuous release or the occurrence of an intermittent release. Such information will enable the facility owner or operator to compile data that will establish trends in releases from a given unit(s) as well as to identify releases from other sources.

Monitoring programs should characterize contaminant releases as a function of time. Climatologic factors such as frequency of intense rainfall, added effects of snowmelt, temperature extremes, and mixing in lakes and estuaries should be evaluated and quantified as causative agents for intermittent contaminant release.

Important concepts to consider in designing the monitoring program for surface water to help meet the above-stated objectives are described below.

13.4.1.1 Phased Characterization

The initial phase of a surface water release characterization program may be directed toward verification of the occurrence of a release identified as suspected by the regulatory agency. It may also serve as the first step for characterizing surface water systems and releases to those systems in cases where a release has already been verified.

The initial characterization will typically be a short-duration activity, done in concert with evaluation of other media that may either transport contaminants to surface waters, or may themselves be affected by discharges from surface waters (i.e., inter-media transport). It may be particularly difficult to define intermittent discharges in the initial characterization effort, especially if the contaminants from these releases are transient in the surface water body.

If the waste characterization is adequate, the initial characterization phase may rely upon monitoring constituents and suitable indicator parameters to aid in defining the nature, rate, and extent of a release. Subsequent phases of release characterization will normally take the form of an expanded environmental monitoring program and hydrologic evaluation, sensitive to seasonal variations in contaminant release and loading to the receiving water bodies, as well as to natural variation in hydrologic characteristics (e.g., flow velocity and volume, stream cross section).

13.4.1.2 Development of Conceptual Model

To effectively design a monitoring program, it is important to develop a conceptual model or understanding of the fate of constituents of the release in the receiving water body. This conceptual understanding will assist in answering the following questions.

- What portion of the receiving water body will be affected by the release and what conditions (e.g., low flow, immediate stormwater runoff) represent reasonable worst case conditions under which sampling should occur?

- What should the relative concentrations of contaminants be at specific receptor points within the water body (e.g., public water supply intakes downstream of a site)?

- How does the release of concern relate to background contamination in the receiving water body as a result of other discharges?

- How might the monitoring program be optimized, based on contaminant dispersion and relative concentrations within the receiving water body?

The fate of waste constituents entering surface waters is highly dependent on the hydrologic characteristics of the various classifications of water bodies, (i.e., streams and rivers, lakes and impoundments, wetlands, and estuaries, as discussed earlier). Because of their complexity, methods for characterization of contaminant fate in wetlands and estuaries is not presented in detail in this guidance. The reader is referred to Mills (1985) for further detail on characterizing contaminant fate in wetlands and estuaries.

13.4.1.3 Contaminant Concentration vs Contaminant Loading

Concentration and loading are different means of expressing contaminant levels in a release or receiving water body. The concept is important in the selection of constituents for monitoring. Both concentration and loading should be

evaluated with respect to the release and the receiving waters. Basing an evaluation solely on concentration may obscure the actual events. In addition, it is essential to quantify individual sources of contaminants and the relationships between media, as well as the loading found in the receiving water body, to effectively define the nature and extent of the contaminant release.

Contaminant concentrations in receiving waters have specific value in interpreting the level of health or environmental effects anticipated from the release. Contaminant loading provides a common denominator for comparison of contaminant inputs between monitoring points. In addition, especially in the case of contaminants that are persistent in sediments (e.g., heavy metals), loadings are a convenient means of expressing ongoing contributions from a specific discharge. The distinction between concentration and loading is best drawn through the following example.

A sample collected from a stream just upgradient of a site boundary (Station A) has a concentration of 50 micrograms per liter (µg/l) of chromium. A second sample collected just downstream of the site (Station B) has a chromium concentration of 45 µg/l. From these data it appears that the site is not releasing additional chromium to the stream. If, however, the stream flow is increasing between these two sampling locations, a different interpretation is apparent. If the stream flow at the upstream location is 1,000 gallons per minute (gpm) and the downstream location is 1,300 gpm, the actual loading of chromium to the stream at the two locations is as follows:

<u>Station A</u>

Chromium = (50.0 µg/l)(1,000 gal/min)(10^{-9} kg/µg)(60 min/hr)(3.785 l/gal) = 0.0114 kg/hr

<u>Station B</u>

Chromium = (45.0 µg/l)(1,300 gal/min)(10^{-9} kg/µg)(60 min/hr)(3.785 l/gal) = 0.0133 kg/hr

It is now apparent that somewhere between the two sampling stations is a source(s) contributing 0.0019 kg/hr of chromium. If all of the flow difference (i.e.,

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300 gpm) is from a single source, then this source would have a chromium concentration of 27.9 µg/l:

Chromium = [(0.0019 kg/hr)(10^9 µg/kg)(1hr/60min)(1 min/300 gal)(1 gal/3.785 l)] = 27.9 µg/l

If, however, 90 percent of this flow difference (i.e., 270 gpm) was due to ground-water discharge with a chromium concentration below detectable limits and the remaining 10 percent (i.e., 30 gpm) was the result of a direct discharge from the facility, this discharge could have a chromium concentration of 279 µg/l.

13.4.1.4 Contaminant Dispersion Concepts

Contaminant dispersion concepts and models of constituent fate can be used to define constituents to be monitored and the location and frequency of monitoring. Dispersion may occur in streams, stratified lakes or reservoirs, and in estuaries. Dispersion may be continuous, seasonal, daily, or a combination of these.

The discussion below is based on information contained in the Draft Superfund Exposure Assessment Manual (EPA, 1987) relative to simplified models useful in surface water fate analyses. The reader is directed to that document for a more in-depth discussion of models. The equations presented below are based on the mixing zone concept originally developed for EPA's National Pollutant Discharge Elimination System (NPDES) under the Clean Water Act. To avoid confusion over regulatory application of these concepts in the NPDES program, and the approach presented below (basically to aid in the development of a monitoring program), the following discussion refers to use of the "Dispersion Zone".

The following equation provides an approximate estimate of the concentration of a substance downstream from a point source release, after dilution in the water body:

$$C_r = \frac{C_u Q_u + C_w Q_w}{Q_u + Q_w}$$

where:

C_r = downstream concentration of substance following complete dispersion (mass/volume)

C_u = upstream concentration of substance before effluent release point (mass/volume)

C_w = concentration of substance in effluent (mass/volume)

Q_w = effluent flow rate (volume/time)

Q_u = upstream flow rate before effluent release point (volume/time)

The following equation may be used to estimate instream concentrations after dilution in situations where waste constituents are introduced via inter-media transfer or from a non-point source, or where the release rate is known in terms of mass per unit time, rather than per unit effluent volume:

$$C = \frac{T_r + M_u}{Q_t}$$

where:

T_r = inter-media transfer rate (mass/time)

M_u = upstream mass discharge rate (mass/time)

Q_t = stream flow rate after inter-media transfer or non-point source release (volume/time)

The above two equations assume the following:

- Dispersion is instantaneous and complete;
- The waste constituent is conserved (i.e., all decay or removal processes are disregarded); and
- Stream flow and rate of contaminant release to the stream are constant (i.e., steady-state conditions).

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For a certain area downstream of the point of release, the assumption of complete dispersion may not be valid. Under certain situations, the dispersion zone can extend downstream for a considerable distance, and concentrations can be considerably higher within the dispersion zone than those estimated by the equation. The length of this zone can be approximated by the following equation:

$$DZ = \frac{0.4\ w^2 u}{0.6\ d\sqrt{gds}}$$

where:

DZ	=	dispersion zone length (length units)
w	=	width of the water body (length units)
u	=	stream velocity (length/time)
d	=	stream depth (length units)
s	=	slope (gradient) of the stream channel (length/length)
g	=	acceleration due to gravity (32 ft/sec^2)

Within the dispersion zone, contaminant concentrations will show spatial variation. Near the release point the contaminant will be restricted (for a discharge along one shoreline) to the nearshore area and (depending on the way the discharge is introduced and its density) can be vertically confined. As the water moves downstream, the contaminant will disperse within surrounding ambient water and the plume will widen and deepen. Concentrations will generally decrease along the plume centerline and the concentration gradients away from the centerline will decrease. Eventually, as described above, the contaminant will become fully dispersed within the stream; downstream from this point concentration will be constant throughout the stream cross-section, assuming that the stream flow rate remains constant.

It is important to understand this concentration variability within the dispersion zone if measurements are to be made near the release. Relatively straightforward analytical expressions (See Neely, 1982) are available to calculate the spatial variation of concentration as a function of such parameters as stream width, depth, velocity, and dispersion coefficients. Dispersion coefficients characterize the dispersion between the stream water and contaminated influx;

they can, in turn, be estimated from stream characteristics such as depth, gradient, and path (i.e., straight or bends).

The above considerations are for instream concentrations resulting from the releases of concern. If total instream concentrations are required, the concentrations determined from background water samples should also be considered. In addition, if introduction of the contaminant occurs over a fixed stream reach, as mig : be the case with a non-point discharge, it should be assumed that the dispersion zone begins at the furthest downstream point within this reach.

13.4.1.5 Conservative vs Non-Conservative Species

The expressions presented thus far have assumed that the contaminant(s) of concern is conservative (i.e., that the mass loading of the contaminant is affected only by the mechanical process of dilution). For contaminants that are non-conservative, the above equations would provide a conservative estimate of contaminant loading at the point of interest within the receiving water body.

In cases where the concentration after dilution of a non-conservative substance is still expected to be above a level of concern, it may be useful to estimate the distance downstream where the concentration will remain above this level and at selected points in between. The reader is referred to the Draft Superfund Exposure Assessment Manual (EPA, 1987), for details regarding this estimation procedure and to specific State Water Quality Standards for determination of acceptable instream concentrations.

13.4.2 Monitoring Constituents and Indicator Parameters

13.4.2.1 Hazardous Constituents

The facility owner or operator should propose a list of constituents and indicator parameters, if appropriate, to be included in the Surface Water investigation. This list should be based on a site-specific understanding of the composition of the release source(s) and the operative release mechanisms, as well as the physical and chemical characteristics of the various classes of contaminants. These factors, as well as potential release mechanisms and migration pathways,

have been discussed in Sections 13.3 and 13.4.1. Also refer to Sections 3 and 7 of this guidance, and to the lists of constituents provided in Appendix B.

13.4.2.2 Indicator Parameters

Indicator parameters (e.g., chemical and biochemical oxygen demand, pH, total suspended solids, etc.) may also play a useful role in release characterization. Though indicators can provide useful data for release verification and characterization, specific hazardous constituent concentrations should always be monitored. Furthermore, many highly toxic constituents may not be detected by indicators because they do not represent a significant amount of the measurement.

Following are brief synopses of some common indicator parameters and field tests that can be used in investigations of surface water contamination. The use of biomonitoring as an indicator of contamination is discussed in Section 13.4.5.

Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD)--BOD is an estimate of the amount of oxygen required for the biochemical degradation of organic material (carbonaceous demand) and the oxygen used to oxidize inorganic material such as sulfides and ferrous iron. It may also measure the oxygen used to oxidize reduced forms of nitrogen (nitrogenous demand) unless their oxidation is prevented by an inhibitor. Because the complete stabilization of a BOD sample may require an extended period, 5 days has been accepted as the standard incubation period. While BOD measures only biodegradable organics, non-biodegradable materials can exert a demand on the available oxygen in an aquatic environment. COD measures the total oxygen demand produced by biological and chemical oxidation of waste constituents. Availability of results for the COD in approximately 4 hours, versus 5 days for the BOD, may be an important advantage of its use in characterizing releases of a transient nature.

COD values are essentially equivalent to BOD when the oxidizable materials present consist exclusively of organic matter. COD values exceed BOD values when non-biodegradable materials that are susceptible to oxidation are present. The reverse is not often the case; however, refinery wastes provide a notable exception. There are some organic compounds, such as pulp and paper mill cellulose, that are non-biodegradable, yet oxidizable. Nitrogenous compounds, which may place a

significant drain on available oxygen in aquatic environments, are not measured in the COD test. In addition, chlorides interfere with the COD test, leading to overestimates of the actual COD. BOD/COD ratios, as an indicator of biodegradability, are discussed in Section 9 (Soil). BOD and COD may be useful indicator parameters if the release is due primarily to degradable organic wastes.

Total Organic Carbon (TOC)--Total organic carbon is valuable as a rapid estimator of organic contamination in a receiving water. TOC, however, is not specific to a given contaminant or even to specific classes of organics. In addition, TOC measurements have little use if the release is primarily due to inorganic wastes.

Dissolved Oxygen (DO)--Measurements of DO may be readily made in the field with an electronic DO meter, which has virtually replaced laboratory titrations. Especially in lake environments, it is valuable to know the DO profile with depth. The bottoms of lakes are often associated with anoxic conditions (absence of oxygen) because of the lack of mixing with the surface and reduced or non-existent photosynthesis. Influx of a contaminant load with a high oxygen demand can further exacerbate oxygen deficiencies under such conditions. In addition, low DO levels favor reduction, rather than oxidation reactions, thus altering products of chemical degradation of contaminants. DO levels less than 3 mg/liter (ppm) are considered stressful to most aquatic vertebrates (e.g., fish and amphibians).

pH--pH is probably one of the most common field measurements made of surface waters. It is defined as the inverse log of the hydrogen ion concentration of an aqueous medium. pH is generally measured in the field with analog or digital electronic pH meters.

As an indicator of water pollution, pH is important for two reasons:

- The range within which most aquatic life forms are tolerant is usually quite narrow. Thus, this factor has significant implications in terms of impact to aquatic communities; and

- The pH of a solution may be a determining factor in moderating other constituent reactions.

Temperature--Along with pH, temperature is a fundamental parameter that should always be recorded in the field when a water sample is collected. Temperature is most often measured by electronic meters that can simultaneously record pH and/or specific conductance. Temperature is a significant parameter because:

- Most aquatic species are sensitive to elevated temperatures;
- Elevated temperatures can be an indication of a contaminant plume;
- Most chemical reactions are temperature-dependent; and
- Temperature defines strata in thermally-stratified lakes.

Alkalinity--Alkalinity is the capacity of water to resist a depression in pH. It is, therefore, a measure of the ability of the water to accept hydrogen ions without resulting in creation of an acid medium. Most natural waters have substantial buffering capacity (a resistance to any alteration in pH, toward either the alkaline or acid side) through dissolution of carbonate-bearing minerals, creating a carbonate/bicarbonate buffer system.

Alkalinity is usually expressed in calcium carbonate ($CaCO_3$) equivalents and is the sum of alkalinities provided by the carbonate, bicarbonate, and hydroxide ions present in solution. Alkalinities in the natural environment usually range from 45 to 200 milligrams per liter (mg/l). Some limestone streams have extremely high buffering capacities, while other natural streams are very lightly buffered and are extremely sensitive to acid (or alkaline) loadings.

Hardness--The sum of carbonate and bicarbonate alkalinities is also termed carbonate hardness. Hardness is generally considered a measure of the total concentration of calcium and magnesium ions present in solution, expressed as $CaCO_3$ equivalents.

Calcium and magnesium ions play a role in plant and animal uptake of contaminants; knowledge of the hardness of a surface water is necessary for evaluation of the site-specific bioaccumulative potential of certain contaminants (e.g., heavy metals).

Total Solids--Analytically, the total solids (TS) content of a water is that remaining after evaporation at 103-115° C or 180°C, depending on the method. The residue remaining represents a sum of the suspended, colloidal, and dissolved solids. Hazardous constituents with high vapor pressures (i.e., volatiles, semi-volatiles) will not remain after evaporation, and will not contribute to the TS determination.

Suspended Solids--Suspended solids are those materials that will not pass a glass-fiber filter. Suspended solids contain both organic and inorganic compounds. For the purpose of comparison to water samples, the average domestic wastewater contains about 200 ppm (mg/l) of suspended solids.

Volatile Suspended Solids--Volatile suspended solids are the volatile organic portion of the suspended solids. Volatile suspended solids are the components of suspended solids that volatilize at a temperature of 600° C. The residue or ash is termed fixed suspended solids and is a measure of the inorganic fraction (i.e., mineral content). The only inorganic salt that will degrade below 600° C is magnesium carbonate.

Total Dissolved Solids--Total dissolved solids context is obtained by subtracting suspended solids from total solids. Its significance lies in the fact that it cannot be removed from a surface water or effluent stream through physical means or simple chemical processes, such as coagulation.

Salinity--The major salts contributing to salinity are sodium chloride (NaCl) and sulfates of magnesium and calcium ($MgSO_4$, $CaSO_4$). The following represents an example of classification of saline waters on the basis of salt content.

Type of Water	Total Dissolved Solids (As Salts)
brackish	1,000 to 35,000 mg/l
seawater	35,000 mg/l
brine	>35,000 mg/l

Specific Conductance--Conductivity measures the capacity to conduct current. Its counterpart is, of course, resistance, measured in ohms. The unit of conductivity has been defined as the mho. Specific conductance is conductivity/unit length. The most common units for specific conductance are mho/cm. Specific conductance can be

measured instantaneously with electronic conductivity meters to comparatively high levels of accuracy and precision in the field and is an excellent real-time indicator parameter.

Conductivity generally rises with increased concentration of dissolved (ionic) species. Therefore, waters with high salinities, or high total dissolved solids, can be expected to exhibit high conductivities. Variations in specific conductance within a stream reach or a portion of an impoundment may indicate the presence of contaminant release points.

Major Ion Chemistry--The nature and prevalence of ionic species may serve as indicators of pollution from waste sources containing inorganics. Ions result from the dissociation of metal salts. The cation (e.g., Na^+, Ca^+, Mg^{++}) is typically a metallic species and the anion (e.g., Cl^-, SO_4^{--}) a non-metallic species.

A common approach to use of ion chemistry as an indicator of waste contamination in surface waters is to analyze for anions. Standard Methods (American Public Health Association, 1985), protocol no. 429 includes the following common anions as analytes:

Chloride (Cl^-)
Fluoride (F^-)
Bromide (Br^-)
Nitrate (NO_3^-)
Nitrite (NO_2^-)
Phosphate (PO_4^{---})
Sulfate (SO_4^{--})

While elevated concentrations of these anions may indicate the presence of inorganic constituents or other contaminants, no information will be provided regarding the identity of specific constituents or contaminants. In addition, elevated levels of anions may be associated with effluent from domestic refuse and/or runoff from fertilized agricultural fields.

The nature and concentrations of naturally-occurring ions in surface waters are a function of the geologic setting of the area, and may be temporarily affected by stormwater runoff, which may cause resuspension of streambed sediments.

In reference to their inertness with respect to constituent and biological degradation, ionic species are termed "conservative." The fact that their mass is not altered (i.e., is conserved) in surface waters permits them to be used in simple dilution modeling.

13.4.3 Selection of Monitoring Locations

The selection of monitoring locations should be addressed prior to sample acquisition because it may affect the selection of monitoring equipment and because monitoring locations will affect the representativeness of samples taken during the monitoring program. Samples must be taken at locations representative of the water body or positions in the water body with specific physical or chemical characteristics. As discussed in Section 13.4.1.2 (Development of Conceptual Model), one of the most important preliminary steps in defining monitoring locations in a surface water monitoring program is developing a conceptual model of the manner in which the release is distributed within the receiving water body. This is dependent on the physical and chemical characteristics of the receiving water, the point source or non-point source nature of the discharge, and the characteristics of the constituents themselves.

As a practical example, if a release contains contaminants whose specific gravities exceed that of water, it may behave almost as a separate phase within the receiving water body, traveling along the bottom of the water body. As another example, certain contaminants may be found in comparatively low concentrations in sediments or within the water column, yet may accumulate in aquatic biota via bioaccumulation. In this case monitoring of the biota would be advised. If the facility owner or operator is unaware of these phenomena, it would be possible for the monitoring program to show no evidence of contamination.

In general, it will be desirable to locate monitoring stations in three areas relative to the discharge in question:

- Background monitoring stations:

Background monitoring should be performed in an area known not to be influenced by the release of concern (e.g., upstream of a release).

- Monitoring stations at the release point(s) or area:

If the release is a point source or area source, periodic monitoring should be performed at monitoring stations near the discharge origin to determine the range of contaminant concentrations. The contaminant stream (e.g., leachate seep, runoff) should also be subjected to monitoring.

- Monitoring of the receiving water body within the area of influence:

One means of evaluating the water quality effects of a discharge is to monitor the discharge point and model its dispersion (e.g., using dispersion zone concepts discussed previously) within the receiving water body. The results of this modeling may be used to determine appropriate sampling locations. Actual sampling of the area thought to be influenced by the release is required. The "area of influence" may be defined as that portion of the receiving water within which the discharge would show a measurable effect. As described previously, the area to be sampled is generally defined in a phased fashion, based on a growing base of monitoring data. It is usually prudent to start with a conservatively large area and continually refine its boundaries. This is particularly true where sensitive receptors (e.g., public water supply intakes, sensitive wetlands, recreation areas) lie downstream of the release. In addition, in order to determine the full extent of the release (and its effects), samples should be taken at locations beyond the perceived area of influence.

The majority of the effort of the monitoring program will take place within the area of influence, as defined above. Many factors are involved in selecting monitoring stations within this area, the most critical being:

- The homogeneity of the water body in terms of temperature, flow, salinity, and other physical and chemical characteristics;

- The representativeness of the monitoring point, in terms of both contaminant characteristics and use factors;

- The presence of areas of pronounced water quality degradation; and

- Defensible monitoring design, including the choice of the monitoring scheme (random, stratified random, systematic, etc.), the experimental design, and adequate sample size determination.

Estuarine areas are particularly difficult in terms of selecting monitoring locations that will allow an adequate evaluation of constituent distribution, because detailed knowledge of the hydrologic characteristics of the estuary is required to accurately locate representative monitoring points. Freshwater - salt water stratification is a particularly important consideration. If stratification is known to occur or is suspected, sampling should be conducted at a range of depths within the estuary as well as at surface locations.

The selection of sampling locations is described in much greater detail in EPA (1973, 1982).

13.4.4 Monitoring Schedule

The monitoring schedule or frequency should be a function of the type of release (i.e., intermittent vs continuous), variability in water quality of the receiving water body (possibly as a result of other sources), stream flow conditions, and other factors causing the release (e.g., meteorological or process design factors). Therefore, frequency of monitoring should be determined by the facility owner or operator on a site-specific basis. Sampling points with common monitoring

objectives should be sampled as close to simultaneously as possible, regardless of the monitoring frequency established.

Factors important in determining the required frequency of monitoring include:

- The homogeneity of the receiving water in terms of factors that may affect the fate of constituents. The most important of these are flow and seasonal or diurnal stratification.

- The characteristics of the releases. Releases may be continuous or event-associated.

As an example, continuous, point source releases of low variability subject to few, if any, additional releases may require relatively infrequent monitoring. On the other hand, releases known to be related to recurrent causes, such as rainfall and runoff, may require monitoring associated with the event. Such monitoring is termed "event" sampling. To evaluate the threshold event required to trigger sampling, as well as the required duration of the monitoring following the event, it is necessary that the role of the event in creating a release from the unit be well understood. In what is probably a very common example, if stormwater runoff is the event of concern, a hydrograph for various storm return intervals and durations should be estimated for the point or area of interest and the magnitude and duration of its effects evaluated.

Continuous monitoring can be accomplished through in situ probes that provide frequent input to field data storage units. However, continuous monitoring is feasible only for the limited number of constituents and indicator parameters for which reliable automatic sampling/recording equipment is available.

In estuaries, samples are generally required through a tidal cycle. Two sets of samples are taken from an area on a given day, one at ebb or flood slack water and another at three hours earlier or later at half tide interval. Sampling is scheduled such that the mid-sampling time of each run coincides with the calculated occurrence of the tidal condition.

Where investigating discharges of contaminated ground water to streams or rivers, it is important to sample during low flow conditions (e.g., using State critical low flow designations) to better assess the possible effects of the release(s) of concern.

13.4.5 Hydrologic Monitoring

The monitoring program should also include provisions for hydrologic monitoring. Specifically, the program should provide for collection of data on the hydrologic condition of the surface water body at the time of sampling.

For example, some indication of the stage and discharge of a stream being monitored needs to be recorded at the time and location each water sample is collected. Similarly, for sampling that occurs during storms, a record of rainfall intensity over the duration of the storm needs to be obtained. Without this complementary hydrologic data, misinterpretation of the water quality data in terms of contaminant sources and the extent of contamination is possible.

The techniques for hydrologic monitoring that could be included in a monitoring program range in complexity from use of simple qualitative descriptions of streamflow to permanent installation of continuously-recording stream gages. The techniques appropriate in a given case will depend on the characteristics of the unit and of the surface waters being investigated. Guidance on hydrologic monitoring techniques can be found in the references cited in Section 13.6.1.

13.4.6 The Role of Biomonitoring

The effects of contaminants may be reflected in the population density, species composition and diversity, physiological condition, and metabolic rates of aquatic organisms and communities. Biomonitoring techniques can provide an effective complement to detailed chemical analyses for identifying chemical contamination of water bodies. They may be especially useful in those cases where releases involve constituents with a high propensity to bioaccumulate. This includes most metal species and organics with a high bioconcentration factor (e.g., >10) or a high octanol/water partition coefficient (e.g., ≥ 2.3). These properties were discussed in Section 13.3.

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Biomonitoring techniques may include:

- Community ecology studies;
- Evaluation of food chain/sensitive species impacts; and
- Bioassays.

These techniques are discussed below.

13.4.6.1 Community Ecology Studies

Indicator species are useful for evaluating the well-being of an aquatic community that may be stressed by the release of contaminants. For example, the condition of the benthic macroinvertebrate community is commonly used as an indicator of the presence of contaminants. The objective of studying the naturally-occurring biological community is to determine community structure that would be expected, in an undisturbed habitat. If significant changes occur, perturbations in the community ecology may be linked to the disturbance associated with release of contaminants to the water body.

EPA is engaged in research to develop rapid bioassessment techniques using benthic macroinvertebrates. Although protocols are being considered, in general these techniques suffer from lack of data on undisturbed aquatic communities and associated water quality information. For some areas (e.g., fisheries), however, indices to community health based on benthic invertebrate communities are available (Hilsenhoff 1982, Cummins and Wilgbach, 1985).

Because species diversity is a commonly-used indicator of the overall health of a community, depressed community diversity may be considered an indicator of contamination. For example, if a release to surface waters has a high chemical oxygen demand (COD) and, therefore, depresses oxygen levels in the receiving water body, the number of different species of organisms that can colonize the water body may be reduced. In this case the oxygen-sensitive species (e.g., the mayfly), is lost from the community and is replaced by more tolerant species. The number of tolerant species is small, but the number of individuals within these species that can colonize the oxygen-deficient waters may be quite large. Therefore,

the overall species diversity could be low, even though the numbers of organisms may be high.

Evaluations of community ecology should however, be sensitive to the role that habitat variability may play in altering community structure. Diversity of habitat may be altered by natural physical conditions (e.g., a rapid increase in stream gradient), substrate characteristics (e.g., silty versus rocky substrate), and so forth. It may also be difficult to directly link contaminant levels with the presence or absence of aquatic organisms, unless there is a secondary impact that is more self-evident, such as high oxygen demand, turbidity, or salinity.

13.4.6.2 Evaluation of Food Chain Sensitive/Species Impacts

At this level of biomonitoring, the emphasis is actually on the threat to specific fish or wildlife species, or man, as a result of bioaccumulation of constituents from the release being carried through the food web. Bioaccumulative contaminants are not rapidly eliminated by biological processes and accumulate in certain organs or body tissues. Their effect may not be felt by individual organisms that initially consume the contaminated substrate or take up the contaminants from the water. However, organisms at higher trophic levels consume the organisms of the lower trophic levels. Consequently, contaminants may become bioaccumulated in organisms and biomagnified through the food web.

Examination of the potential for bioaccumulation and biomagnification of contaminants requires at least a cursory characterization of the community to define its trophic structure, that is, which organisms occupy which relative positions within the community. Based on this definition, organisms representative of the various trophic levels may be collected, sacrificed, and analyzed to determine the levels of the contaminants of interest present.

If a specific trophic level is of concern, it may be possible to short-cut the process by selectively collecting and analyzing organisms from that level for the contaminants of concern. This may be the case, for instance, if certain organisms are taken by man either commercially or through recreational fishing, for consumption. It may also be necessary to focus on the prey of special-status fish or wildlife (e.g., eagles and other birds of prey) to establish their potential for

exposure. This type of biomonitoring may be especially useful if constituents released have a relatively high potential to bioaccumulate. A discussion of indicators that are generally predictive of constituents which have a significant potential for bioaccumulation was presented in Section 13.3.

In addition, in the selection of organisms it is important to consider the ability of a given organism to accumulate a class of contaminants and the residential vs migratory nature of the organisms. For example, bullfrogs are superior for accumulating metals but poor for organics; spawning (thus migratory) salmon would be much less useful for characterizing a release from a local facility than would resident fish.

13.4.6.3 Bioassay

Bioassay may be defined as the study of specially selected representative species to determine their response to the release of concern, or to specific constituents of the release. The organisms are "monitored" for a period of time established by the bioassay method. The objective of bioassay testing is to establish a concentration-response relationship between the contaminants of concern and representative biota that can be used to evaluate the effects of the release. Bioassay testing may involve the use of indigenous organisms (U.S. EPA, 1973) or organisms available commercially for this purpose. Bioassays have an advantage over strict constituent analyses of surface waters and effluents in that they measure the total effect of all constituents within the release on aquatic organisms (within the limits of the test). Such results, therefore, are not as tightly constrained by assumptions of contaminant interactions. Discussions of bioassay procedures are provided by Peltier and Weber (1985) and Horning and Weber (1985).

The criterion commonly used to establish the endpoint for a bioassay is mortality of the test organisms, although other factors such as depressed growth rate, reproductive success, behavior alteration, and flesh tainting (in fish and shellfish) can be used. Results are commonly reported as the LC50 (i.e., the lethal concentration that resulted in 50 percent mortality of the test organisms within the time frame of the test) or the EC50 (i.e., the effective concentration that resulted in 50 percent of the test organisms having an effect other than death within the time frame of the test).

One potential use of bioassays during the RFI is to predict the effect of a release on sensitive species residing in the affected surface water(s). Bioassay may be especially useful if the release is intermittent. In this case, samples of the waste may be taken from the unit of concern and used to conduct bioassay tests. The bioassay may be conducted using the waste at 100 percent strength, and in diluted form, to obtain a concentration response relationship. The results of this testing may then be used to predict the effects of a release on the surface water biota.

Bioassays can serve as important complements to the overall monitoring program. In considering the role and design of bioassays in a monitoring program, the facility owner or operator should be aware of the advantages and limitations of toxicity testing. The study design must account for factors such as species sensitivity and frequency of monitoring which may be different from the considerations that feed into chemical monitoring programs. Toxicity testing techniques are an integral part of the Clean Water Act program to control the discharge of toxic substances. Many issues associated with toxicity testing have been addressed in this context in the Technical Support Document for Water Quality-Based Toxics Control (Brandes et al, 1985).

13.5 Data Management and Presentation

The owner or operator will be required to report on the progress of the RFI at appropriate intervals during the investigation. The data should be reported in a clear and concise manner, and interpretations should be supported by the data. The following data presentation methods are suggested for the various phases of the surface water investigation. Further information on the various procedures is given in Section 5. Section 5 also provides guidance on various reports that may be required.

13.5.1 Waste and Unit Characterization

Waste and unit characteristics should be presented as:

- Tables of waste constituents, concentrations, effluent flow and mass loadings;

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- Tables of relevant physical and chemical properties of potential contaminants (e.g., solubility);

- Narrative description of unit operations;

- Surface map and plan drawings of facility, unit(s), and surface waters; and

- Identification of "reasonable worst case" contaminant release to surface waters.

13.5.2 Environmental Setting Characterization

The environment of the waste unit(s) and surface waters should be described in terms of physical and biological environments in the vicinity. This description should include:

- A map of the area portraying the location of the waste unit in relation to potential receiving waters;

- A map or narrative classification of surface waters (e.g., type of surface water, uses of the surface water, and State classification, if any);

- A description of the climatological setting as it may affect the surface hydrology or release of contaminants; and

- A narrative description of the hydrologic conditions during sampling periods.

13.5.3 Characterization of the Release

The complex nature of the data involving multiple monitoring events, monitoring locations, matrices (water, sediment, biota), and analytes lends itself to graphic presentation. The most basic presentation is a site map or series of maps

that locate the monitoring stations for each monitoring event. These maps may also be adapted to include isopleths for specific analytes; however, since the isopleths imply a continuity within their borders, they may not be appropriate unless they are based on an adequate number of monitoring points and representative data. The contours should be based on unit intervals whose accuracy ranges do not overlap. In most situations, two separate reporting formats are appropriate. First, the data should be included as tables. These tables should generally be used to present the analytical results for a given sample. Each table could include samples from several locations for a given matrix, or could include samples from each location for all sample matrices. Data from these tables can then be summarized for comparison purposes using graphs.

Graphs are most useful for displaying spatial and temporal variations. Spatial variability for a given analyte can be displayed using bar graphs where the vertical axis represents concentration and the horizontal axis represents downstream distance from the discharge. The results from each monitoring station can then be presented as a concentration bar. Stacked bar graphs can be used to display these data from each matrix at a given location or for more than one analyte from each sample.

Similarly, these types of graphs can be used to demonstrate temporal variability if the horizontal axis represents time rather than distance. In this configuration, each graph will present the results of one analyte from a single monitoring location. Stacked bars can then display multiple analytes or locations. Line graphs, like isopleths, should be used cautiously because the line implies a continuity, either spatial or temporal, that may not be accurately supported by the data.

Scatter plots are useful for displaying correlations between variables. They can be used to support the validity of indicator parameters by plotting the indicator results against the results for a specific constituent.

Graphs are used to display trends and correlations. They should not be used to replace data tables, but rather to enhance the meaning of the data.

13.6 Field and Other Methods

The purpose of this section is to provide an overview of methods that can be used to characterize the nature, rate, and extent of contaminant releases to surface water. Detailed descriptions of specific methods can be found in the indicated references.

The methods presented in this section relate to four specific areas, as follows:

- Surface Water Hydrology;
- Sampling and Constituent Analysis of Surface Water, Sediments, and Biota;
- Characterization of the Condition of the Aquatic Community; and
- Bioassay Methods.

13.6.1 Surface Water Hydrology

The physical attributes of the potentially affected water body should be characterized to effectively develop a monitoring program and to interpret results. Depending on the characteristics of the release and the environmental setting, any or all of the following hydrologic measurements may need to be undertaken.

- Overland flow:
  - Hydraulic measurement;
  - Rainfall/runoff measurement;
  - Infiltration measurement; and
  - Drainage basin characterization (including topographic characteristics, soils and geology, and land use).

- Open channel flow:
  - Measurement of stage (gaging activities);
  - Measurement of width, depth, and cross-sectional area;
  - Measurement of velocity;

- Measurement of channel discharge;
  - Measurement of channel discharge at controls (e.g., dams and weirs); and
  - Definition of flow pathways - solute dispersion studies.

- Closed conduit flow:
  - Measurement of discharge.

- Lakes and impoundments:
  - Morphometric mapping;
  - Bathymetric mapping;
  - Temperature distributions; and
  - Flow pathways.

The following references provide descriptions of the measurements described above.

National Oceanic and Atmospheric Administration. Rainfall Atlas of the U.S.

Viessman, et al., 1977. Introduction to Hydrology.

USGS. 1977. National Handbook of Recommended Methods for Water-Data Acquisition Chapter 1 (Surface Water) and Chapter 7 (Physical Basin Characteristics for Hydrologic Analyses).

U.S Department of Interior. 1981. Water Measurement Manual. Bureau of Reclamation. GPO No. 024-003-00158-9. Washington, D.C.

Chow. 1964. Open Channel Hydraulics. McGraw-Hill. New York, N.Y.

In addition, the following monographs in the Techniques of Water Resources Investigations series of the USGS (USGS-WSP-1822, 1982) give the reader more detailed information on techniques for measuring discharge and other characteristics of various water bodies and hydrologic conditions:

Benson and Dalrymple. 1967. General Field and Office Procedures for Indirect Discharge Measurement.

Bodhaine, 1968. Measurement of Peak Discharge at Culverts by Indirect Methods. USGS-TWI-03-AS.

Buchanan and Somers. 1968. Stage Measurements at Gaging Stations.

Carter and Davidian. 1968. General Procedure for Gaging Streams. USGS-TWI-03-AL.

13.6.2 Sampling of Surface Water, Runoff, Sediment, and Biota

13.6.2.1 Surface Water

The means of collecting water samples is a function of the classification of the water body, as discussed in Section 13.3.3.1. The following discussion treats lakes and impoundments separately from streams and rivers although, as indicated below, the actual sampling methods are similar in some cases. Wetlands are considered an intergrade between these waters. Stormwater and snowmelt runoff is also treated as a separate category (Section 13.6.2.2). Although estuaries also represent somewhat of an intergrade, estuary sampling methods are similar to those for large rivers and lakes.

13.6.2.1.1 Streams and Rivers

These waters represent a continuum from ephemeral to intermittent to perennial. Streams and rivers may exhibit some of the same characteristics as lakes and impoundments. The degree to which they are similar is normally a function of channel configuration (e.g., depth, cross sectional area and discharge rate). Larger rivers are probably more similar to most lakes and impoundments, with respect to sampling methods, than to free-flowing headwater streams. In general, however, streams and rivers exhibit a greater degree of mixing due to their free-flowing characteristics than can be achieved in lakes and impoundments. Mixing and dilution of inflow can be slow to fast, depending on the point of discharge to the stream or river and the flow conditions.

Stream and river sampling methods do not differ appreciably from those outlined in the following section (Lakes and Impoundments). However, the selection of monitoring stations must consider additional factors created by differential flow velocities within the stream cross section. Strong currents and turbulence as a result of channel configuration may affect the amount of mixing and the distribution of contaminants in the stream. The reader may wish to refer to the references provided in Section 13.3.1 for a discussion of the manner in which differential velocities are handled in stream gaging studies to obtain representative discharge measurements.

13.6.2.1.2 Lakes and Impoundments

These waters are, by definition, areas where flow velocity is reduced, limiting the circulation of waters from sources such as discharging streams or ground water. They often include a shoreline wetland where water circulation is slow, dilution of inflowing contaminants is minimal, and sediments and plant life become significant factors in sampling strategies. The deeper zones of open water may be vertically stratified and subject to periodic turnover, especially in temperate climates. Sampling programs should be designed to obtain depth-specific information as well as to characterize seasonal variations.

Access to necessary monitoring stations may be impeded by both water depth and lush emergent or floating aquatic vegetation, requiring the use of a floating sampling platform or other means to appropriately place the sampling apparatus. It is common to employ rigid extensions of monitoring equipment to collect surface samples at distances of up to 30 or 40 feet from the shoreline. However, a boat is usually the preferred alternative for distances over about six feet. A peristaltic pump may also be used to withdraw water samples, and has the added advantage of being able to extract samples to a depth of 20 to 30 feet below the surface.

Many sampling devices are available in several materials. Samples for trace metals should not be collected in metal bottles, and samples for organics should not be collected in plastic bottles. Teflon or Teflon-coated sampling equipment, including bottles, is generally acceptable for both types of constituents. EPA (1982) and EPA (1986) provide an analysis of the advantages and disadvantages of many

sampling bottles for specific sampling situations. Detailed descriptions of the use of dippers/transfer devices, pond samplers, peristaltic pumps, and Kemmerer bottles are provided by EPA (1984).

Depth-specific samples in lake environments are usually collected with equipment such as Kemmerer bottles (commonly constructed of brass), Van Dorn samplers (typically of polyvinyl chloride or PVC construction), or Nansen tubes. The depth-specific sample closure mechanism on these devices is tripped by dropping a weight (messenger) down the line. Kemmerer bottles and Nansen tubes may also be outfitted with a thermometer that records the temperature of the water at the time of collection.

13.6.2.1.3 Additional Information

Additional information regarding specific surface water sampling methods may be found in the following general references:

U.S. EPA. 1986. Methods for Evaluating Solid Wastes. EPA/SW-846. GPO No. 955-001-00000-1. Office of Solid Waste. Washington, D.C. 20460.

U.S. EPA. 1984. Characterization of Hazardous Waste Sites -- A Methods Manual: Volume II. Available Sampling Methods. EPA-600/4-84-076. NTIS PB-168771. Washington, D.C. 20460.

U.S. EPA. 1986. Handbook of Stream Sampling for Wasteload Allocation Applications. EPA/625/6-83/013.

U.S. EPA. 1982. Handbook for Sampling and Sample Preservation of Water and Wastewater. NTIS PB 83-124503.

USGS. 1977. National Handbook of Recommended Methods for Water-Data Acquisition.

13.6.2.2 Runoff Sampling

Runoff resulting from precipitation or snowmelt creates an intermittent release situation that requires special treatment for effective sampling. The contaminant release mechanism in runoff situations may be overflow of ponds containing contaminants or erosion of contaminated soils. Based on an evaluation of the waste characteristics and the environmental setting, the facility owner or operator can determine whether waste constituents will be susceptible to this release mechanism and migration pathway.

Once it has been determined that erosion of contaminated soils is of concern, the quantity of soil transported to any point of interest, such as the receiving water body, can be determined through application of an appropriate modification of the Universal Soil Loss Equation (USLE). The USLE was initially developed by the U.S. Department of Agriculture, Agricultural Stabilization and Conservation Service (ASCS) to assist in the prediction of soil loss from agricultural areas. The initial formula is reproduced below:

$$A = RKLSCP$$

where:

A	=	Estimated annual average soil loss (tons/acre)
R	=	Rainfall intensity factor
K	=	Soil erodibility factor
L	=	Slope-length factor
S	=	Slope-gradient factor
C	=	Cropping management factor*
P	=	Erosion control practice factor*

*C and P factors can be assumed to equal unity in the equation if no specific crop or erosion management practices are currently being employed. Otherwise, these factors can be significantly less than unity, depending on crop or erosion control practices.

Section 2.6 (Soil Contamination) of the Draft Superfund Exposure Assessment Manual (EPA, 1987) provides a discussion of the application of a modified USLE to characterization of releases through soil erosion. This discussion is summarized in Appendix H (Soil Loss Calculation).

If the potential for a significant contaminant release exists, based on analysis of the hydrologic situation and waste site characteristics, event samples should be taken during high runoff periods. In situations where high runoff is predictable, such as spring runoff or the summer thundershower season, automatic samplers may be set to sample during these periods. Perhaps the most effective way to ensure sampling during significant events is to have personnel available to collect samples at intervals throughout and following the storm. Flow data should be collected coincident with sample collection to permit calculation of contaminant loading in the runoff at various flows during the period. Automated sampling equipment is available that will collect individual samples and composite them either over time or with flow amount, with the latter being preferred. Flow-proportional samplers are usually installed with a flow-measuring device, such as a weir with a continuous head recorder. Such devices are readily available from commercial manufacturers and can be rented or leased. Many facilities with an NPDES discharge permit routinely use this equipment in compliance monitoring.

Automated samplers are discussed in Section 8 of Handbook for Sampling and Sample Preservation of Water and Wastewater (EPA, 1982) (NTIS PB 83-124503); this publication also includes other references to automated samplers and a table of devices available from various manufacturers.

13.6.2.3 Sediment

Sediment is traditionally defined as the deposited material underlying a body of water. Sediment is formed as waterborne solids (particulates) settle out of the water column and build up as bottom deposits.

Sedimentation is greatest in areas where the stream velocity decreases, such as behind dams and flow control structures, and at the inner edge of bends in stream channels. Sediments also build up where smaller, fast-flowing streams and runoff discharge into larger streams and lakes. These areas can be important investigative

areas. Some sections of a streambed may be virtually without sediments. In some streams or some areas of streams, water velocity may be too fast for sediments to deposit and actually may scour the bottom, transporting material and depositing it further downstream. The stream bed in such an area will be primarily rocks and debris.

In some situations, such as low-flow conditions, the overlying water temporarily recedes, exposing sediments to the air. Runoff channels, small lakes, and small streams and rivers may on occasion dry completely. In these cases, samples can be collected using the same procedures described in the Soils section (Section 9) of this document.

For this discussion, the definition of sediment will be expanded to include any material that may be overlain by water at any time during the year. This definition then includes what may otherwise be considered submerged soils and sludges. Submerged soils are found in wetlands and marshes. They may be located on the margins of lakes, ponds, and streams, or may be isolated features resulting from collected runoff, or may appear in areas where the ground-water table exists at or very near the land surface. In any instance they are important investigative areas.

Sludges are included for discussion here because many RCRA facilities use impoundments for treatment or storage and these impoundments generally have a sludge layer on the bottom. Sampling these sludges involves much the same equipment and techniques as would be used for sediments.

There are essentially two ways to collect sediment samples, either by coring or with grab/dredges. Corers are metal tubes with sharpened lower edges. The corer is forced vertically into the sediment. Sediments are held in the core tube by friction as the corer is carefully withdrawn; they can then be transferred to a sample container. There are many types and modifications of corers available. Some units are designed to be forced into the sediments by hand or hydraulic pressure; others are outfitted with weights and fins and are designed to free fall through the water column and are driven into the sediment by their fall-force.

Corers sample a greater thickness of sediments than do grab/dredges and can provide a profile of the sediment layers. However, they sample a relatively small

surface area. Most corers are less than four inches in diameter and are more commonly two inches in diameter.

Grab/dredges are basically clamshell-type scoops that sample a larger surface area but offer less depth of penetration. Typical grab/dredge designs are the Ponar, Eckman, and Peterson versions; each has a somewhat different operating mechanism and slightly different advantages. Some use spring force to close the jaws while others are counter-levered like ice tongs.

In sediment sampling, vertical profiling is not normally required because deposition of hazardous material is often a recent activity in terms of sedimentary processes. Grab/dredges that sample a greater surface area may be more appropriate than corers. Similarly, shallow sludge layers contained in surface impoundments should be sampled with grab/dredges because corer penetration could damage the impoundment liner, if present. Thicker sludge layers which may be present in surface impoundments, may be sampled using coring equipment if it is important to obtain vertical profile information.

Submerged soils are generally easier to sample with a corer, than with a grab/dredge because vegetation and roots can prevent the grab/dredges from sealing completely. Under these conditions, most of the sample may wash out of the device as it is recovered. Corers can often be forced through the vegetation and roots to provide a sample. In shallow water, which may overlie submerged soils, sampling personnel can wade through the water (using proper equipment and precautions) and choose sample locations in the small, clear areas between vegetative stems and roots.

A wide variety of sampling devices are available for collection of sediment samples. Each has advantages and disadvantages in a given situation, and a variety of manufacturers produce different versions of the same device. As with water sampling, it is important to remember that metal samplers should not be used when collecting samples for trace metal analysis, and sampling devices with plastic components should not be used when collecting samples for analysis of organics.

The following references describe the availability and field use of sediment samplers:

U.S. EPA. 1982. Handbook for Sampling and Sample Preservation of Water and Wastewater. Environmental Monitoring and Support Laboratory, EPA-600/4-82-029. NTIS PB 83-124503.

U.S. EPA. 1985. Methods Manual for Bottom Sediment Sample Collection. NTIS PB 86-107414.

USGS. 1977, update June 1983. National Handbook of Recommended Methods for Water-Data Acquisition.

U.S. EPA. 1984. Characterization of Hazardous Waste Sites -- A Methods Manual: Volume II. Available Sampling Methods. EPA-600/4-84-076. NTIS PB 85-168771.

13.6.2.4 Biota

Collection of biota for constituent analysis (whole body or tissue) may be necessary to evaluate exposure of aquatic organisms or man to bioaccumulative contaminants. For the most part, collection should be restricted to representative fish species and sessile macroinvertebrates, such as mollusks. Mollusks are filter-feeders; bioaccumulative contaminants in the water column will be extracted and concentrated in their tissues. Fish species may be selected on the basis of their commercial or recreational value, and their resultant probability of being consumed by man or by special status-species of fish or wildlife.

The literature on sampling aquatic organisms is extensive. Most sampling methods include capture techniques that be collected using sampling bottles (as for water samples) or nets of appropriate mesh sizes. Periphyton may be most easily collected by scraping off the substrate to which the organisms are attached. Other techniques using artificial substrates are available if a quantitative approach is required. Aquatic macroinvertebrates may be collected using a wide variety of methods, depending on the area being sampled; collection by hand or using forceps may be efficient. Grab sampling, sieving devices, artificial substrates and drift nets may also be used effectively. EPA (1973) provides a discussion of these techniques, as well as a method comparison and description of data analysis techniques.

Fish collection techniques may be characterized generally as follows (USGS, 1977):

- Entangling gear:
  Gill nets and trammel nets.
- Entrapping gear:
  Hoop nets, basket traps, trap nets, and fyke and wing nets.
- Encircling gear:
  Haul seine, purse seine, bay seine, and Danish seine.
- Electroshocking gear:
  Boat shockers, backpack shockers, and electric seines.

Selection of sampling equipment is dependent on the characteristics of the water body, such as size and conditions, the size of the fish to be collected, and the overall objectives of the study. Fisheries Techniques (Nielsen and Johnson, 1983) and Guidelines for Sampling Fish in Inland Waters (Backiel and Welcomme, 1980) provide basic descriptions of sampling methods and data interpretation from fisheries studies.

13.6.3 Characterization of the Condition of the Aquatic Community

Evaluation of the condition of aquatic communities may proceed from two directions. The first consists of examining the structure of the lower trophic levels as an indication of the overall health of the aquatic ecosystem. With respect to RFI studies, a healthy water body would be one whose trophic structure indicates that it is not impacted by contaminants. The second approach focuses on a particular group or species, possibly because of its commercial or recreational importance or because a substantial historic data base already exists.

The first approach emphasizes the base of the aquatic food chain, and may involve studies of plankton (microscopic flora and fauna), periphyton (including bacteria, yeast, molds, algae, and protozoa), macrophyton (aquatic plants), and benthic macroinvertebrates (e.g., insects, annelid worms, mollusks, flatworms, roundworms, and crustaceans). These lower levels of the aquatic community are

studied to determine whether they exhibit any evidence of stress. If the community appears to have been disturbed, the objective is to characterize the source(s) of the stress and, specifically, to focus on the degree to which the release of waste constituents has caused the disturbance or possibly exacerbated an existing problem. An example of the latter would be the further depletion of already low dissolved oxygen levels in the hypolimnion of a lake or impoundment through the introduction of waste with a high COD and specific gravity.

The sampling methods referenced in Section 13.6.2.4 may be adapted (by using them in a quantitative sampling scheme) to collect the data necessary to characterize aquatic communities. Hynes (1970) and Hutchinson (1967) provide an overview of the ecological structure of aquatic communities.

Benthic macroinvertebrates are commonly used in studies of aquatic communities. These organisms usually occupy a position near the base of the food chain. Just as importantly, however, their range within the aquatic environment is restricted, so that their community structure may be referenced to a particular stream reach or portion of lake substrate. By comparison, fish are generally mobile within the aquatic environment, and evidence of stress or contaminant load may not be amenable to interpretation with reference to specific releases.

The presence or absence of particular benthic macroinvertebrate species, sometimes referred to as "indicator species," may provide evidence of a response to environmental stress. Several references are available in this regard. For more information, the reader may consult Selected Bibliography on the Toxicology of the Benthic Invertebrates and Periphyton (EPA, 1984).

A "species diversity index" provides a quantitative measure of the degree of stress within the aquatic community, and is an example of a common basis for interpretation of the results of studies of aquatic biological communities. The following equation (the Sannon-Wiener Index) demonstrates the concept of the diversity index:

$$H = \sum_{i=1}^{S} (Pi)(\log_2 Pi)$$

where:

H = species diversity index
s = number of species
Pi = proportion of total sample belonging to the ith species

Measures of species diversity are most useful for comparison of streams with similar hydrologic characteristics or for the analysis of trends over time within a single stream. Additional detail regarding the application of other measures of community structure may be found in the following references:

U.S. EPA. 1973. Biological Field and Laboratory Methods for Measuring the Quality of Surface Water and Effluents.

USGS. 1977, Update May, 1983. National Handbook of Recommended Methods of Water-Data Acquisition.

Curns, J. Jr., and K.L. Dickson, eds. 1973. ASTM STP 528: Biological Methods for the Assessment of Water Quality. American Society for Testing and Materials. STP528. Philadelphia, PA.

The second approach to evaluating the condition of an aquatic community is through selective sampling of specific organisms, most commonly fish, and evaluation of standard "condition factors" (e.g., length, weight, girth). In many cases, receiving water bodies are recreational fisheries, monitored by state or federal agencies. In such cases, it is common to find some historical record of the condition of the fish population, and it may be possible to correlate operational records at the waste management facility with alterations in the status of the fish population.

Sampling of fish populations to evaluate condition factors employs the same methodologies referenced in Section 13.6.2.4. Because of the intensity of the effort usually associated with obtaining a representative sample of fish, it is common to coordinate tissue sampling for constituent analysis with fishery surveys.

13.6.4 Bioassay Methods

The purpose of a bioassay, as discussed is more detail in Section 13.4.6.3, is to predict the response of aquatic organisms to specific changes within the environment. In the RFI context, a bioassay may be used to predict the potential adverse environmental effects of releases to surface water. Thus, bioassay is not generally considered to be an environmental characterization or monitoring technique. As indicated below, bioassay may be required for Federal water quality programs or state programs, especially where stream classification (e.g., warm-water fishery, cold-water fishery) is involved.

Bioassays may be conducted on any aquatic organism including algae, periphyton, macroinvertebrates, or fish. Bioassay includes two main techniques, acute toxicity tests and chronic toxicity tests. Each of these may be done in a laboratory setting or using a mobile field laboratory. Following is a brief discussion of acute and chronic bioassay tests.

Acute Toxicity Tests--Acute toxicity tests are used in the NPDES permit program to identify effluents containing toxic wastes discharged in toxic amounts. The data are used to predict potential acute and chronic toxicity in the receiving water, based on the LC50 and appropriate dilution, and application of persistence factors. Two types of tests are used; static and flow-through. The selection of the test type will depend on the objectives of the test, the available resources, the requirements of the test organisms, and effluent characteristics. Special environmental requirements of some organisms may preclude static testing.

It should be noted that a negative result from an acute toxicity test with a given effluent sample does not preclude the presence of chronic toxicity, nor does it negate the possibility that the effluent may be acutely toxic under different conditions, such as variations in temperature or contaminant loadings.

There are many sources of information relative to the performance of acute bioassays. Methods for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms (Peltier and Weber, 1985) provides a comprehensive treatment of the subject.

Chronic Toxicity Tests--Chronic toxicity tests may include measurement of effluent effects on growth and reproductive success. These tests usually require long periods of time, depending on the life cycles of the test organisms. Chronic bioassays are generally relatively sophisticated procedures and are more intensive in terms of manpower, time and expense than are acute toxicity tests. The inherent complexity of these tests dictate careful planning with the regulatory agency prior to initiation of the work. Methods for Measuring the Chronic Toxicity of Effluents to Aquatic Organisms (Horning and Weber, 1985) is a companion volume to the methods document noted above, and contains method references for chronic toxicity tests. A discussion of bioassay procedures is also provided in Protocol for Bioassessment of Hazardous Waste Sites, NTIS PB 83-241737. (Tetra Tech, 1983).

Chronic toxicity tests are also used in the NPDES permit program to identify and control effluents containing toxic wastes in toxic amounts.

13.7 Site Remediation

Although the RFI Guidance is not intended to provide detailed guidance on site remediation, it should be recognized that certain data collection activities that may be necessary for a Corrective Measures Study may be collected during the RFI. EPA has developed a practical guide for assessing and remediating contaminated sites that directs users toward technical support, potential data requirements and technologies that may be applicable to EPA programs such as RCRA and CERCLA. The reference for this guide is provided below.

U.S. EPA. 1988. Practical Guide for Assessing and Remediating Contaminated Sites. Office of Solid Waste and Emergency Response. Washington, D.C. 20460.

The guide is designed to address releases to ground water as well as soil, surface water and air. A short description of the guide is provided in Section 1.2 (Overall RCRA Corrective Action Process), under the discussion of Corrective Measures Study.

13.8 Checklist

RFI CHECKLIST - SURFACE WATER

Site Name/Location _____

Type of Unit _____

1. Does waste characterization include the following information? (Y/N)
   - Constituents of concern _____
   - Concentrations of constituents _____
   - Mass of the constituent _____
   - Physical state of waste (e.g., solid, liquid, gas) _____
   - Water solubility _____
   - Henry's Law Constant _____
   - Octanol/Water Partition Coefficient (K_{ow}) _____
   - Bioconcentration Factor (BCF) _____
   - Adsorption Coefficient (Koc) _____
   - Physical, biological, and chemical degradation _____

2. Does unit characterization include the following information? (Y/N)
   - Age of unit _____
   - Type of unit _____
   - Operating practices _____
   - Quantities of waste managed _____
   - Presence of cover _____
   - Dimensions of unit _____
   - Presence of natural or engineered barriers _____
   - Release frequency _____
   - Release volume and rate _____
   - Non-point or point source release _____
   - Intermittent or continuous release _____

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RFI CHECKLIST - SURFACE WATER (Continued)

3. Does environmental setting information include the following? (Y/N)

- Areal extent of drainage basin _____
- Location and interconnection of all streams, lakes and other surface water features _____
- Flow identification as ephemeral, intermittent or perennial _____
- Channel alignment, gradient and discharge rate _____
- Flood and channel control structures _____
- Source of lake and impoundment water _____
- Lake and impoundment depths and surface area _____
- Vertical temperature stratification of lakes and impoundments _____
- Wetland presence and role in basin hydrology _____
- NPDES and other discharges _____
- USGS gaging stations or other existing flow monitoring systems _____
- Surface water quality characteristics _____
- Average monthly and annual precipitation values _____
- Average monthly temperature _____
- Average monthly evaporation potential estimates _____
- Storm frequency and severity _____
- Snowfall and snow pack ranges _____

4. Have the following data on the initial phase of the release characterization been collected? (Y/N)

- Monitoring locations _____
- Monitoring constituents and indicator parameters _____
- Monitoring frequency _____
- Monitoring equipment and procedures _____
- Concentrations of constituents and locations at which they were detected _____
- Background monitoring results _____

	(Y/N)
• Hydrologic and biomonitoring results	_____
• Inter-media transfer data	_____
• Analyses of rate and extent of contamination	_____

5. Have the following data on the subsequent phase(s) of the release characterization been collected?

	(Y/N)
• New or relocated monitoring locations	_____
• Constituents and indicators added or deleted for monitoring	_____
• Modifications to monitoring frequency, equipment or procedures	_____
• Concentrations of constituents and locations at which they were detected	_____
• Background monitoring results	_____
• Hydrologic and biomonitoring results	_____
• Inter-media transfer data	_____
• Analyses of rate and extent of contamination	_____

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DRAFT FINAL
(Revised)

AIR RELEASE SCREENING ASSESSMENT METHODOLOGY

MAY 1989

APPENDIX G

AIR RELEASE SCREENING ASSESSMENT METHODOLOGY

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1.0 INTRODUCTION

A screening method has been developed for evaluating which waste management units have air releases warranting further investigation under a RCRA Facility Investigation (RFI). This method can be used as an intermediate step between the general qualitative determination of the RCRA Facility Assessment (RFA) regarding identification of air emissions that warrant an RFI, and the actual performance of a complicated and costly RFI. Specifically, this screening methodology provides a basis for identifying air releases with the potential to have resulted in off-site exposures that meet or exceed health-based criteria in the RFI Guidance.

This screening methodology has been developed as a technical aid for routine use by EPA Regional and State staff who may not be familiar with air release assessments. However, it should also be considered a resource available to prioritize waste management units which may warrant the conduct of an RFI for the air media. Alternative resources (e.g., available air monitoring data, more sophisticated modeling analyses, judgmental factors) may also provide important input to the RFI decision-making process.

The screening methodology itself is explained in Section 2 and example applications of it are presented in Section 3. A discussion of background information that addresses the technical basis for the air release screening methodology is presented in Appendix A.

2.0 SCREENING METHODOLOGY

This section presents the air release screening assessment methodology. This methodology can be used as a transition between the general qualitative determination made in the RFA regarding air emissions that warrant an RFI, and the actual performance of an RFI.

The primary (recommended) screening approach involves the application of available emission rate models and dispersion models. An alternative approach involves the use of technical aids based on scaling modeling results for a limited set of source scenarios.

The screening methodology for releases of organics is based on using the CHEMDAT6 air emission models, available from EPA's Office of Air Quality Planning and Standards (OAQPS), (U.S. EPA, December 1987). Specifically, the following unit categories are directly addressed in this section:

- Disposal impoundments
- Storage impoundments
- Oil Films on Storage Impoundments
- Mechanically Aerated Impoundments
- Diffused Air Systems
- Land treatment (emissions after tilling)
- Oil Film Surfaces on Land Treatment Units
- Closed landfills
- Open landfills
- Wastepiles

The alternative approach presented in this section involves scaling the emission rate results from numerous source scenarios that have been modeled using CHEMDAT6. These scaling computations can become tedious if numerous source scenarios are evaluated. In addition, the direct use of CHEMDAT6 models will provide more representative unit-specific emission estimates. Therefore, it is strongly recommended that EPA Regional and State agency staff develop a capability to use CHEMDAT6 directly to model unit-specific and facility-specific scenarios.

CHEMDAT6 has been developed for use on a microcomputer using LOTUS spreadsheet software; therefore, these models can easily be used by staff familiar with LOTUS applications. However, the basic strategy described in this section to estimate ambient concentrations can still be successfully used even without using LOTUS.

The screening methodology for organic emissions from storage tanks is based on emission factors in EPA's AP-42, "Compilation of Air Pollutant Emission Factors" (U.S. EPA, September 1985). The following categories of tanks are addressed:

- Fixed roof tanks
- Floating roof tanks
- Variable vapor space tanks.

Open tanks should be assessed using the methodology for storage impoundments.

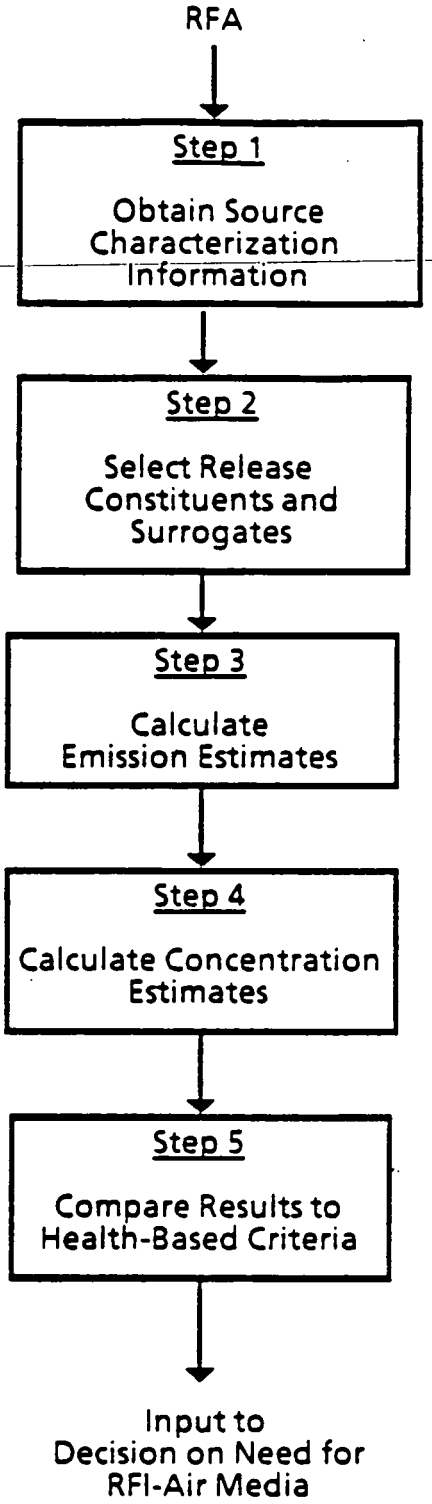
The screening methodology for particulate matter releases from wind erosion of storage piles and batch dumping and loader activity on the pile is based on emission factors in EPA's AP-42 (U.S. EPA, September 1985). The screening methodology for particulate matter releases from wind erosion of flat, exposed, contaminated surface areas is based on emission factors in EPA's "Fugitive Emissions from Integrated Iron and Steel Plants" (U.S. EPA, March 1978). The EPA-OAQPS is currently developing guidance regarding particulate emissions for treatment, storage, and disposal facilities.

2.1 Overview

The air release screening assessment methodology involves applying emission rate and dispersion results to estimate long-term ambient concentrations at receptor locations for comparison to health-based criteria. The methodology consists of five steps as follows (see Figure 2-1):

- Step 1 - Obtain Source Characterization Information: This information (e.g., unit size, operational schedule) is needed to define the emission potential of the specific unit.

FIGURE 2-1
SCREENING METHODOLOGY OVERVIEW



- Step 2- Select Release Constituents and Surrogates: The primary approach involves using the actual physical/chemical properties for all unit-specific constituents for emission modeling purposes. The alternative (scaling) screening approach uses a limited set of constituents or surrogates to represent a wide range of potential release constituents. This surrogate approach significantly simplifies the screening assessment process.

- Step 3 - Calculate Emission Estimates: The primary approach involves the use of emission rate models based on unit-specific source conditions. Modeling results of emission rates for a wide range of source conditions are also presented in Appendices C through Q. As an alternative approach, these modeling results can be interpolated to estimate an emission rate specific to the unit.

- Step 4 - Calculate Concentration Estimates: Emission rates from Step 3 are used to calculate concentration estimates at receptor locations of interest. The primary approach involves the application of dispersion models based on site-specific meteorological conditions. As an alternative approach, dispersion conditions are accounted for by use of modeling results available in Appendix R for typical annual meteorological conditions.

- Step 5 - Compare Concentration Results to Health-Based Criteria: Concentration results from Step 4 can be compared to constituent-specific health-based criteria provided in the RFI Guidance.

For some applications, Step 4 (Calculate Concentration Estimates) will not warrant the use of emission models because it can be assumed that all the volatile wastes handled will eventually be emitted to the air. This assumption is generally appropriate for highly volatile organic compounds placed in a disposal unit like a surface impoundment. In these cases, the air emission rate can be assumed to be equivalent to the disposal rate, so that an emission rate model may not be required. This assumption is valid because of the long-term residence time of wastes in the disposal units. In open units like surface impoundments, a substantial portion of the volatile constituents will frequently be released to the atmosphere within

several days. However, for more complex situations (e.g., storage or treatment units where total volatilization of the constituents is not expected), air emission models can be used to obtain a more refined long-term release rate.

Results from the air release screening assessment, using the above steps, will provide input to decisions on the need for an RFI for the air media. They can also be used to prioritize air emission sources at a facility (i.e., by identification of the major onsite air emission sources) as well as to prioritize the total release potential at candidate facilities.

2.2 Step 1 - Source Characterization Information

Implementation of the air release screening assessment methodology involves collecting source characterization information, as illustrated in Figure 2-2. Specifically, this involves completion of Column 2 of unit-specific Emission Rate Estimation Worksheets (included in Appendix S) as specified in Figure 2-2. Parameters in Column 2 of the worksheet represent standard input used by the CHEMDAT6 air emission models or input to the AP-42 emission equations. Source characterization information should be available from the RFA but it may be necessary to request additional information from the facility owner or operator on an ad hoc basis.

Additional worksheets should be completed for each unit to be evaluated. Similar units can be grouped together and considered as one area source to simplify the assessment process. For example, several contiguous landfills of similar design could be evaluated efficiently as one (combined) source.

Completeness and quality of the source characterization information are very important and, as previously stated, directly affect the usefulness of the screening assessment results. Certain source characterization parameters are considered critical inputs to the screening assessment. These critical input parameters are needed to define the total mass of constituents in the waste input to the unit being evaluated or the potential for release of particles less than 10 microns. These parameters have been identified in the unit-specific worksheet (Tables S-1 through S-13 for VO sources and Tables S-14 and 15 for particulate sources).

FIGURE 2-2
STEP 1 - OBTAIN SOURCE CHARACTERIZATION INFORMATION

RFA

↓

Complete Column 2 of Unit-Specific Emission Rate Estimation Worksheet:

- Disposal impoundment - Table S-1
- Storage impoundment/open tank- Table S-2
- Oil film on storage impoundment - Table S-3
- Mechanically aerated impoundment - Table S-4
- Diffused air system - Table S-5
- Land treatment (emissions after
- tilling) - Table S-6
- Oil film surface on land treatment unit - Table S-7
- Closed landfill - Table S-8
- Open landfill - Table S-9
- Wastepile - Table S-10
- Fixed roof tank - Table S-11
- Floating roof tank - Table S-12
- Variable vapor space tank - Table S-13
- Storage pile (particulates) - Table S-14
- Exposed, flat, contaminated area (particulates) Table S-15

↓

Complete Column 2 of additional worksheets for each unit to be evaluated (similar units can be grouped as one area source).

↓

Select typical and/or reasonable worst-case values specified in Appendices C-M if values for input parameters are not available.

- Disposal impoundment - Table C-1
- Storage impoundment/open tank- Table D-1
- Oil film on storage impoundment - Table E-1
- Mechanically aerated impoundment - Table F-1
- Diffused air system - Table G-1
- Land treatment (emissions after tilling) - Table H-1
- Oil film surface on land treatment unit - Table I-1
- Closed landfill - Table J-1
- Open landfill - Table K-1
- Wastepile - Table L-1
- Fixed roof tank - Table M-1
- Floating roof tank - Table N-1
- Variable vapor space tank - Table O-1
- Storage pile (particulates)- Table P-1
- Exposed, flat, contaminated area (particulates)- Table Q-1

↓

Step 2-

Select Release Constituents and Surrogates

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Unit-specific values for some of the source characterization parameters may be difficult to determine. For example, air porosity values of the fixed waste are needed for evaluating emissions from open landfills, closed landfills, and wastepiles, and total porosity values of the fixed waste are needed to evaluate emissions from open landfills and wastepiles. However, unit-specific data are typically not available for these parameters. If unit-specific values for input parameters are not available, typical and/or reasonable worst-case values should be selected from the range of values specified in Appendices C through Q.

Selection of source scenario input data should be based on realistic physical and chemical limitations. For example, the waste concentration value for a constituent should not exceed the constituent-specific solubility in water.

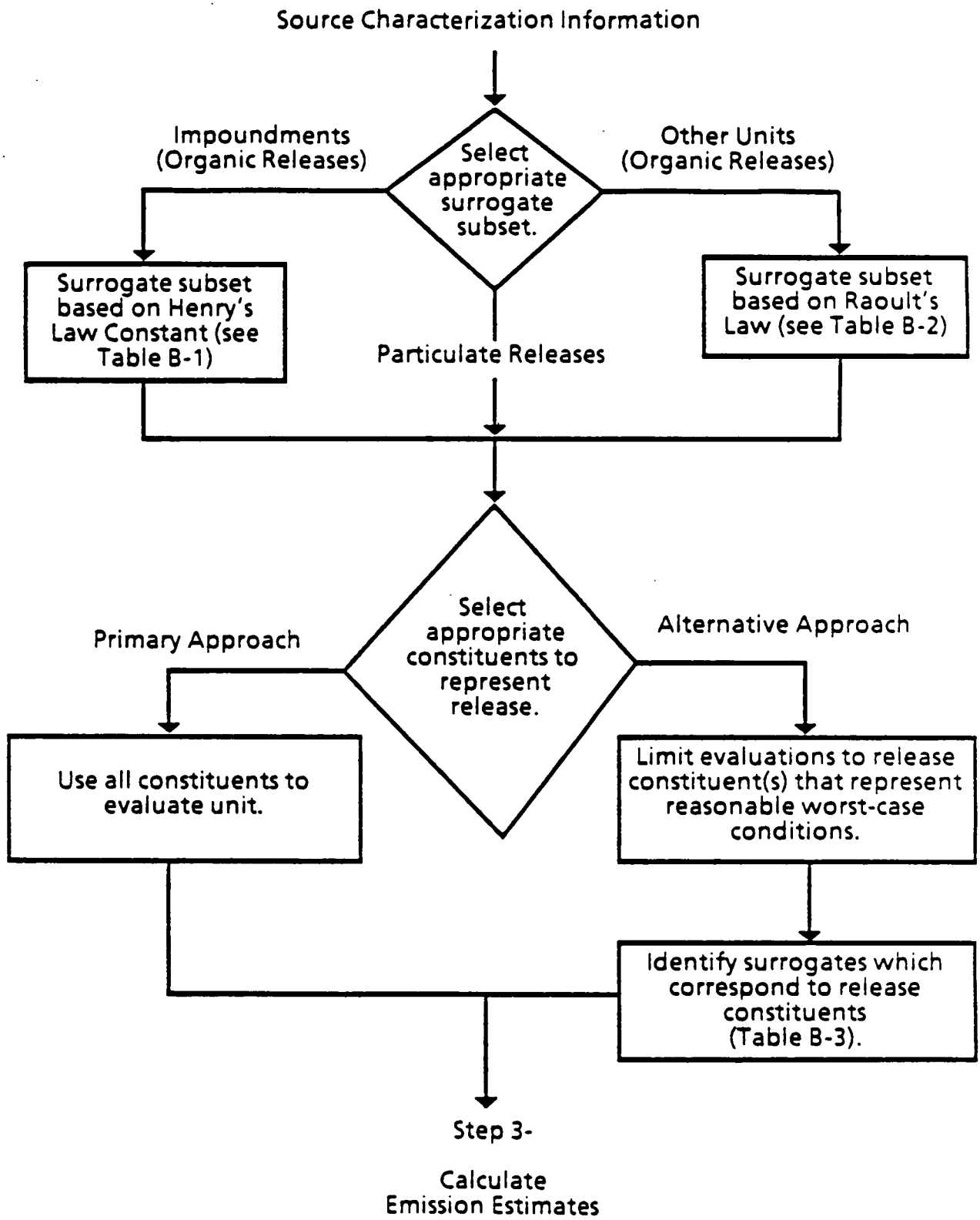
2.3 Step 2 - Release Constituent Surrogates

The primary approach involves using the actual physical/chemical properties for all unit-specific constituents for emission modeling purposes. The alternative screening approach (scaling) uses a limited set of constituents or surrogates.

A limited set of surrogates is used to represent the constituents of concern in this alternative screening method to represent a wide range of potential release constituents. This significantly simplifies the screening assessment process since the list of potential air release constituents included in the RFI Guidance is extensive. Selection of appropriate source release constituent surrogates is illustrated in Figure 2-3. Table B-3 presents the appropriate surrogate to be used for each constituent of concern. This step is not used in screening for particle emissions from storage piles and exposed areas.

Table B-3 of Appendix B, presents the appropriate surrogate to be used for each constituent of concern. Two subsets of surrogates are presented in Appendix B. The first subset is applicable to emissions that can be estimated based on Henry's Law Constant (i.e., applicable for low concentrations, less than 10 percent, of wastes in aqueous solution). Surrogates based on Henry's Law Constant are appropriate for units like storage and disposal impoundments. Henry's Law Constant surrogates are presented in Table B-1.

FIGURE 2-3
STEP 2 - SELECT RELEASE CONSTITUENTS AND SURROGATES



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The second subset is applicable to emissions that can be estimated based on Raoult's Law. Raoult's Law predicts the behavior of most concentrated mixtures of water and organic solvents (i.e., solution with over 10 percent solute). Surrogates based on Raoult's Law are appropriate for units like landfills, wastepiles, land treatment units and storage tanks. Raoult's Law surrogates are listed in Table B-2.

It is also necessary to select surrogates from the appropriate subset (i.e., from the Henry's Law Constant or Raoult's Law subset selected) to represent release constituents of interest. The primary approach is to use all surrogates from the appropriate subset to evaluate the unit. This approach will provide a comprehensive data base for the screening assessment. An alternative approach is to select release constituent(s)/surrogate(s) that represent reasonable worst-case conditions. Release constituents having the most restrictive health-based criteria and those having high volatility are frequently associated with these reasonable worst-case (long-term) release conditions.

2.4 Step 3 - Emission Estimates

Two approaches for calculating emission estimates are identified in Figure 2-4. The primary approach involves the calculation of unit-specific emission rates based on available models (e.g., CHEMDAT6, et cetera). This approach is recommended for most applications.

The alternative approach involves the calculation of emissions by applying scaling factors to emission modeling results presented in Appendices C through Q for a limited set of source scenarios. This approach is appropriate when a rapid preliminary estimate is needed and modeling resources are not available. However, the primary approach will provide more representative unit-specific emission estimates.

Specific instructions for implementing the alternative emission estimation approach are presented in Figure 2-5.

Emission rate modeling results for a wide range of source scenario conditions are presented in Appendices C through Q to facilitate implementation of the alternative emission estimation approach. These available modeling results can be

FIGURE 2-4
STEP 3 - CALCULATE EMISSION ESTIMATES

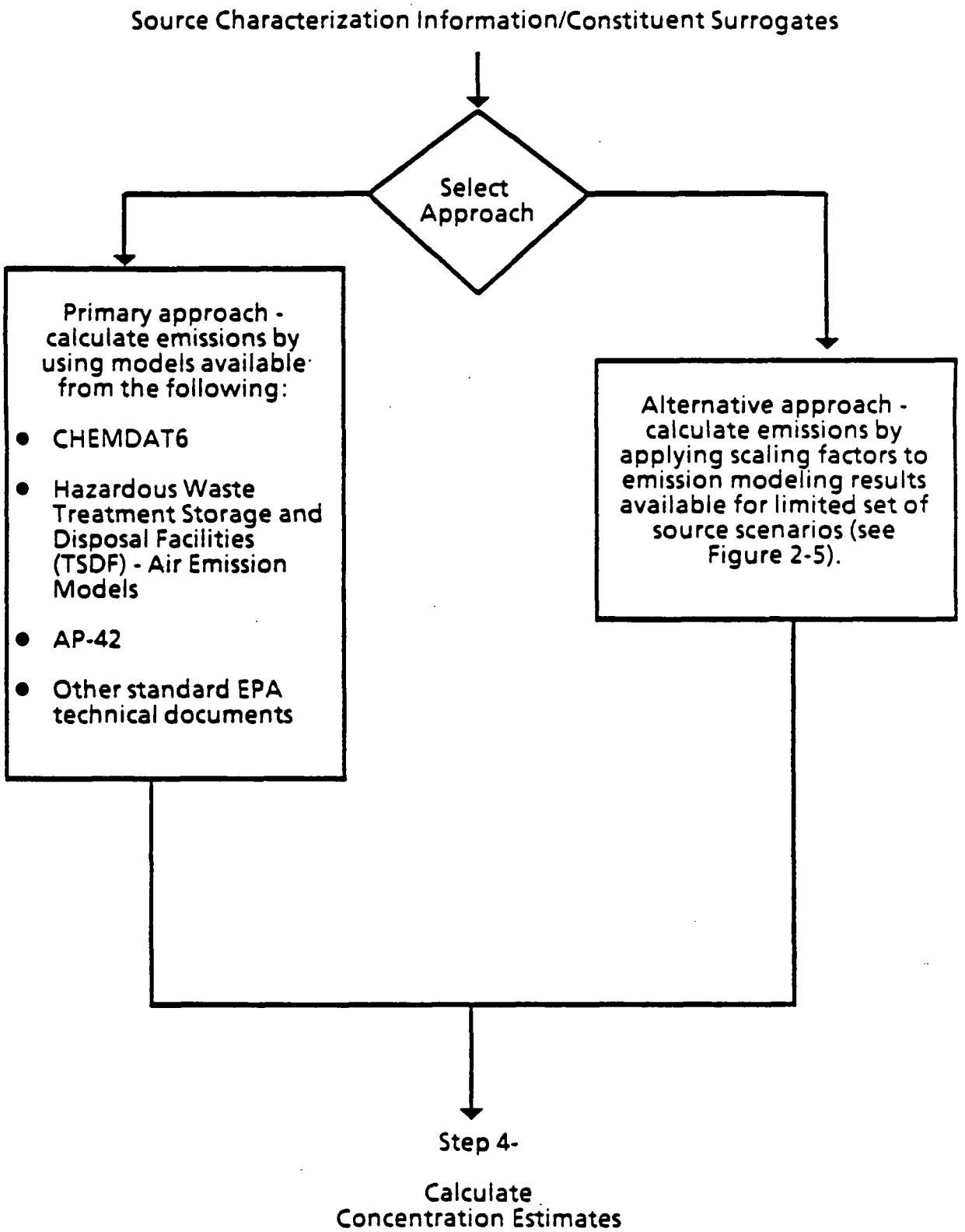


FIGURE 2-5
STEP 3 - CALCULATE EMISSION ESTIMATES (ALTERNATIVE APPROACH)

Source Characterization Information/Constituent Surrogates

↓

Obtain Emission Rate Estimation Worksheets (as selected in Step 1):

- Disposal impoundment - Table S-1
- Storage impoundment/open tank - Table S-2
- Oil film on storage impoundment - Table S-3
- Mechanically aerated impoundment - Table S-4
- Diffused air system - Table S-5
- Land treatment - Table S-6
- Oil film surface on land treatment unit - Table S-7
- Closed landfill - Table S-8
- Open landfill - Table S-9
- Wastepile - Table S-10
- Fixed roof tank - Table S-11
- Floating roof tank - Table S-12
- Variable vapor space tank - Table S-13
- Storage pile (particulates)- Table S-14
- Exposed, flat, contaminated area (particulates) - Table S-15

↓

Select the source scenario for each modeling parameter (identified in Col. 1 of worksheets) that best represents unit-specific conditions from available cases (appropriate alternative case numbers are identified in Col. 3 of the worksheet and case specifications are presented in Appendices C-Q):

- Disposal impoundment - Table C-1
- Storage impoundment/open tank- Table D-1
- Oil film on storage impoundment - Table E-1
- Mechanically aerated impoundment - Table F-1
- Diffused air system - Table G-1
- Land treatment - Table H-1
- Oil film surface on land treatment unit -Table I-2
- Closed landfill - Table J-1
- Open landfill - Table K-1
- Wastepile - Table L-1
- Fixed roof tank - Table M-1
- Floating roof tank - Table N-1
- Variable vapor space tank - Table O-1
- Storage pile (particulates) - Table P-1
- Exposed, flat, contamianted area (particulates) Table Q-1

↓

Compute parameter-specific scaling factors by completing Cols. 4-11 (12 for Raoult's Law surrogates) of the worksheet or Col. 4 for particulate worksheets based on modeling results presented in Appendices C-Q (computational instructions are presented with each worksheet):

- Disposal impoundment - Table C-2
- Storage impoundment/open tank- Table D-2
- Oil film on storage impoundment - Table E-2
- Mechanically aerated impoundment - Table F-2
- Diffused air system - Table G-2
- Land treatment - Table H-2
- Oil film surface on land treatment unit -Table I-2
- Closed landfill - Table J-2
- Open landfill - Table K-2
- Wastepile - Table L-2
- Fixed roof tank - Table M-2
- Floating roof tank - Table N-2
- Variable vapor space tank - Table O-2
- Storage pile (particulates) - Table P-2
- Exposed, flat, contaminated area (particluates) Table Q-2

↓

Complete unit-specific emission rate, which accounts for unit-specific scaling factors (last line item on each worksheet based on instructions presented with each worksheet).

↓

Step 4-

Calculate Concentration Estimates

interpolated to estimate a unit-specific emission rate. The process for calculating emission rate estimates for application to a specific unit (i.e., unit-specific application) is summarized in Figure 2-5.

Calculating emission rate estimates is accomplished by completing an Emission Rate Estimation Worksheet, included in Appendix S. A separate worksheet is provided in Appendix S for each unit category. Column 2 (unit-specific values for each modeling parameter) of the worksheet should already have been completed during Step 1.

The alternative emission estimation approach presented in Figure 2-5 also involves scaling the emission rate modeling results available in Appendices C through Q to represent unit-specific conditions. This is accomplished by first computing individual parameter-specific factors and then combining the results to calculate a unit-specific emission rate for each surrogate of interest. Therefore, it is necessary to select the appropriate source scenario that best represents unit-specific conditions for each modeling parameter (identified in Column 1 of the worksheet). Column 3 of the worksheet identifies the appropriate candidate scenario cases for each parameter. The source scenario case specifications (i.e., values of the modeling parameters for each case) are presented in Table C -1 (disposal impoundment), D-1 (storage impoundment), E-1 (oil film on storage impoundment), F-1 (mechanically aerated impoundment), G-1 (diffused air system), H-1 (land treatment), I-1 (oil film surface on land treatment unit), J-1 (closed landfill), K-1 (open landfill), L-1 (wastepile), M-1 (fixed roof tank), N-1 (floating roof tank), O-1 (variable vapor space tank), P-1 (storage piles), and Q-1 (exposed, flat, contaminated areas).

It is also recommended that a second scenario case be selected for each parameter in order to bracket source conditions. The selection of a second scenario is appropriate if unit-specific source conditions are different than those presented in the source scenario case specifications (Appendices C-Q).

Parameter-specific scaling factors are computed by following instructions in each worksheet and by completing Columns 4-11 (12). (Column 12 is needed for Raoult's Law surrogates.) Information needed to complete Columns 4-11 (12) is available in Appendices C through Q. Information needed to complete worksheets for particulate emissions are available in Appendices P and Q. Instructions for

computing unit-specific emission rates based on applying scaling factors are included in each worksheet.

The last set of three source scenario cases for unit-category modeling results presented in Appendices C through Q represents the following:

- Reasonable best-case emission rate for unit category (for a typical source surface area or tank size)

- Typical emission rate for unit category (for a typical source surface area or tank size)

- Reasonable worst-case emission rate for unit category (for a typical source surface area or tank size)

Frequently these cases can be used to rapidly estimate typical and extreme emission rates. However, they should not be considered as absolute values. These scenarios generally represent the range of source conditions identified in the Hazardous Waste Treatment, Storage and Disposal Facilities (TSDF) Air Emission Models (U.S. EPA, December 1987). But frequently this information was incomplete, and subjective estimates were postulated instead. Therefore, the emission rates for best, typical and worst case source scenarios should only be used as a preliminary basis to compare and prioritize sources.

At times one of the source scenario cases presented in the Appendices may be representative of the modeling parameters for the unit scenario being evaluated. For these situations, it is not necessary to implement all of the intermediate computational steps otherwise needed to complete the worksheet. Instead, the modeling results presented in Appendices C through Q can be used to directly represent unit-specific emission rates. However, it may be necessary to scale these results to account for the unit-specific surface area and waste constituent concentrations. (Scaling can be accomplished by the approach specified in each worksheet).

2.5 Step 4 - Concentration Estimates

Emission rate values from Step 3 are used as input to calculate concentration estimates at receptor locations of interest. Dispersion conditions are accounted for by use of available modeling results for typical annual meteorological conditions. A summary of this process is included in Figure 2-6. Dispersion models can be applied to directly estimate concentration. This primary approach is recommended for most applications. The EPA-Industrial Source Complex (ISC) model is generally appropriate for a wide range of sources in flat or rolling terrain. Alternative models are identified in the Guideline On Air Quality Models (Revised) (U.S. EPA, July 1988).

An alternative approach to obtain concentration estimates (for flat terrain sites) involves the application of dispersion factors presented in Appendix R. A Concentration Estimation Worksheet (Table R-1) is used as the basis for concentration calculations. This approach is appropriate when a rapid preliminary estimate is needed and modeling resources are not available. However, the primary approach will provide more representative site-specific concentration estimates.

Specific instructions for implementing the alternative concentration estimation approach are presented in Figure 2-7.

Concentrations should be estimated at locations corresponding to receptors of concern (pursuant to RFI Guidance). Receptor information may also be available from the RFA. Column 2 of the worksheet should be completed to define distances to receptors as a function of direction.

Ambient concentrations are influenced by atmospheric dispersion conditions in addition to emission rates. Atmospheric dispersion conditions for ground-level non-buoyant releases (as is the case for surface impoundment, landfill, land treatment unit, and wastepile applications) can be accounted for by the use of dispersion factors. Appropriate dispersion factors based on Figure R-1 should be used to complete Column 3 of the worksheet. The dispersion factors presented in Figure R-1 include individual plots for a range of unit-surface-area sizes. Instruction regarding the use of these plots to determine unit- and receptor-specific dispersion factors is included with Figure R-1.

FIGURE 2-6
STEP 4 - CALCULATE CONCENTRATION ESTIMATES

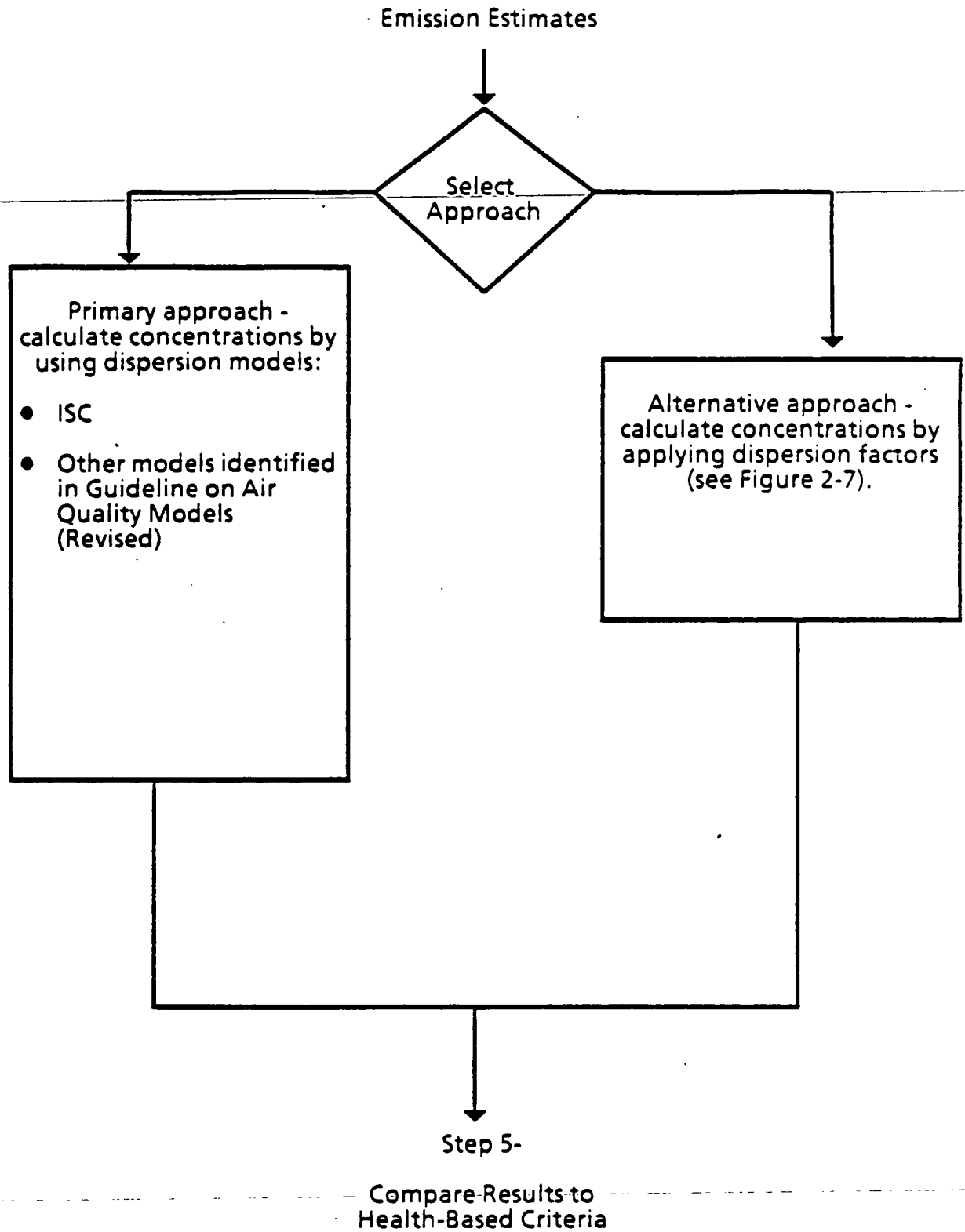
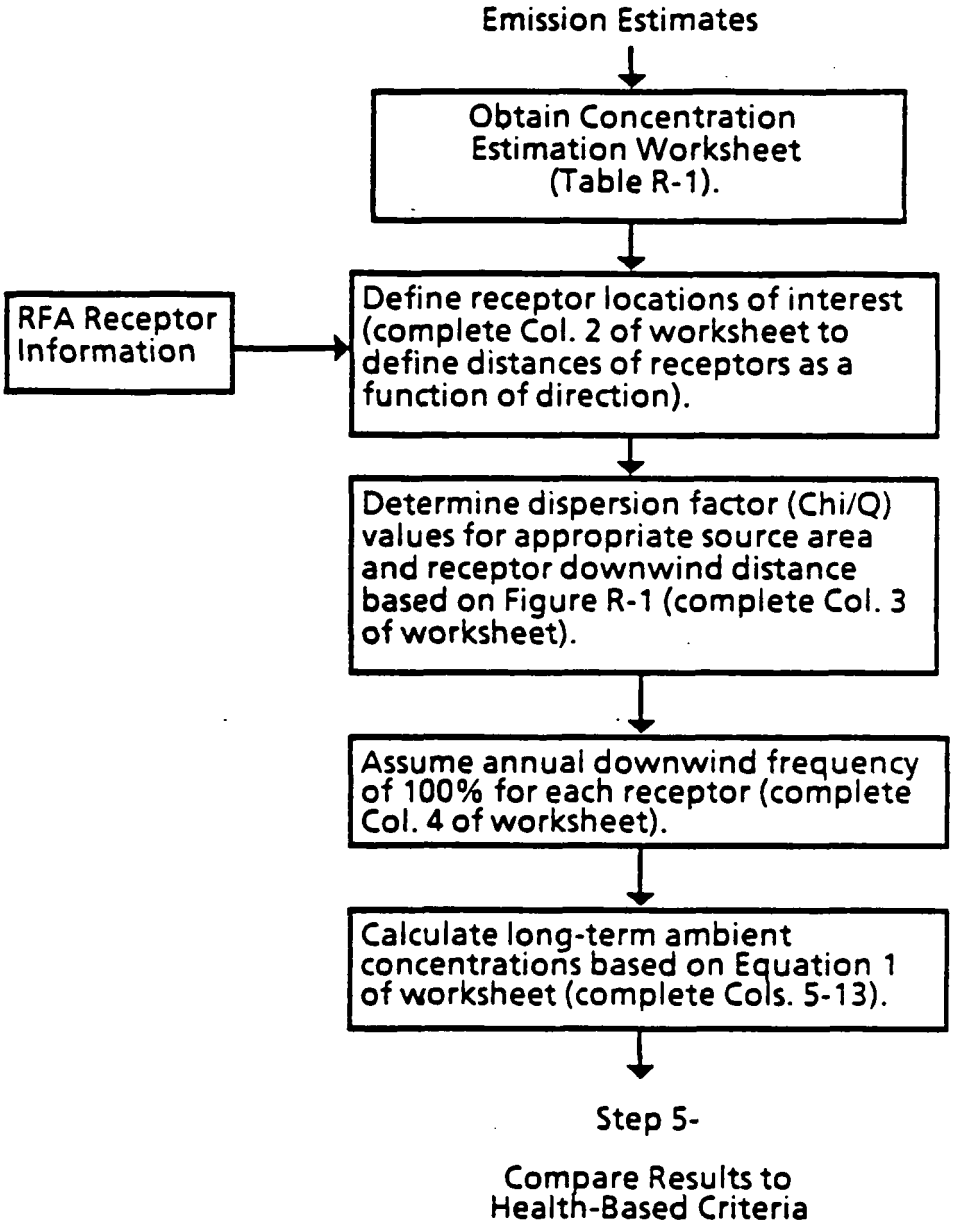


FIGURE 2-7
STEP 4 - CALCULATE CONCENTRATION ESTIMATES
(ALTERNATIVE APPROACH)



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The dispersion factors presented in Figure R-1 are based on the assumption that winds are flowing in one direction (i.e., toward the receptor of interest) 100 percent of the time on an annual basis. This conservative assumption of a wind direction frequency of 100% for each receptor of interest should be used if Figure R-1 is used as the basis to estimate dispersion conditions for Column 4 of the worksheets.

The information entered into Column 3 and 4 of the worksheet, plus the emission rate results calculated during Step 3, provides the required input to calculate ambient concentrations. Specifically, Equation 1 presented in the worksheet should be used to obtain ambient concentrations for each surrogate and receptor location. Equation 1 of Table R-1 includes a safety factor of 10 which is applied to all concentration estimates based on the scaling approach. This factor accounts for the inherent uncertainty involved in the scaling approach. This safety factor is applicable to all concentration estimates based on emission rates obtained via the scaling approach. These results should be entered into Columns 5 through 13 of the worksheet.

2.6 Step 5 - Health Criteria Comparisons

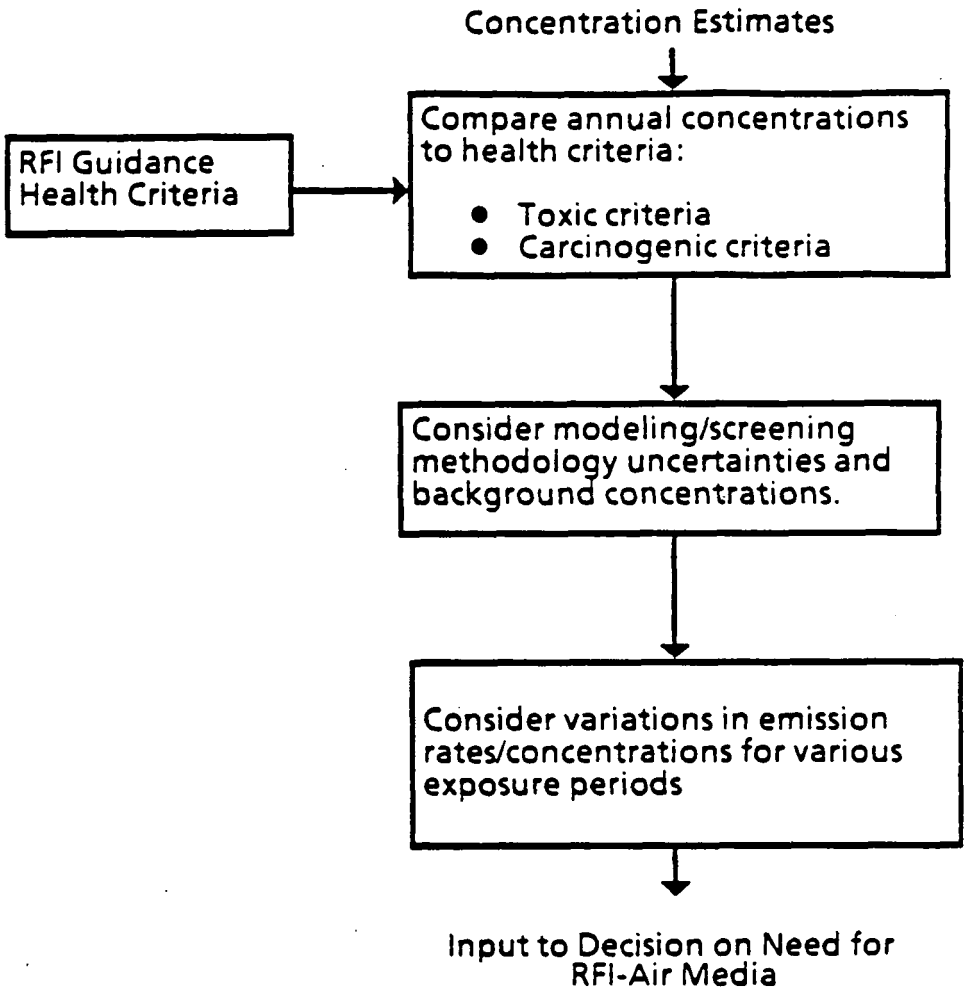
Concentration results from Step 4 can be compared to constituent-specific health-based criteria provided in the RFI Guidance (see Figure 2-8). To facilitate this comparison, it is recommended that the appropriate reference toxic and carcinogenic criteria be entered in the space allocated in the Concentration Estimation Worksheet.

Interpretation of the ambient concentration estimates should also account for the uncertainties associated with the following components of the assessment:

- Inaccuracies in input source characterization data will directly affect concentration results.

- Emission rate models have not been extensively verified. However, OAQPS states, "In general, considering the uncertainty of field emission measurements, agreement between measured and predicted emissions generally agree within an order of magnitude." (U.S. EPA, April 1987). These verifications have been for short-term emission conditions. Model

FIGURE 2-8
STEP 5 - COMPARE RESULTS TO HEALTH-BASED CRITERIA



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performance is expected to be better for long-term emission rate estimation (as used for this screening assessment).

- Inaccuracies associated with use of the alternative emission estimation approach presented in Figure 2-5.

  - Source conditions for the unit of interest may not be the same as those for the source scenarios presented in Appendices C-Q. Therefore, scenarios should be selected to bracket the unit-specific conditions in order to obtain a range of emission rate estimates.

  - The use of scaling factors for each source parameter may yield somewhat different emission rate values compared to those based on direct use of a model with unit-specific inputs. These differences are attributed to the interrelationships of source parameters which may not be linear. A comparison of direct modeling results versus scaling estimates is presented in Exhibit 2-1.

- Atmospheric dispersion models for long-term applications (as used for this screening assessment) typically are accurate within a factor of ± 2 to 3 for flat terrain (inaccuracy can be a factor of ± 10 in complex terrain.

Therefore, "safety factors" commensurate with these uncertainties should be applied to concentration estimates for health criteria comparisons.

The calculations of emission rate and concentration estimates obtained have been for a 1-year period. Some units, such as closed landfills, will have different average emission rates for longer exposure periods for certain constituents. The air pathway health-based criteria included in the RFI Guidance are based on a 70-year exposure period. Appendices C through Q each contain a set of scenario cases for 1-, 5-, 10-, and 70-year exposures for information purposes. However, only inactive units are expected to have an average 70-year emission rate that is significantly different from the 1-year rate. All of the emission results presented in Appendices C through Q are assumed to be active with the exception of closed landfills (Appendix J). Air concentrations for each one-year period within the reference 70 year exposure period should be less than those associated with constituent-specific health criteria.

EXHIBIT 2-1

RATIO OF SCALING ESTIMATES TO CHEMDAT6 EMISSION RATE MODELING RESULTS (FIGURE 2-5)

Unit Type	Reasonable Best Case/Worst Case Emission Rate Scenarios									
	Henry's Law Surrogates:	MHLB	HHLB	LHMB	MHMB	HHMB	LHHB	MHHB	HHHB	--
	Raoult's Law Surrogates:	HVHB	HVMB	HVLB	MVHB	MVMB	MVLB	LVMB	VHVHB	VHVLB
	Particle Case:	Particle	--	--	--	--	--	--	--	
Disposal Impoundment		0.81/1.00	0.81/1.00	0.86/1.04	0.81/1.00	0.81/1.00	0.68/1.03	0.81/1.00	0.81/1.00	--
Storage Impoundment		1.10/1.51	1.00/1.43	1.10/1.50	1.00/1.52	1.10/1.43	0.97/0.79	1.00/1.51	1.00/1.43	--
Oil Film on Storage Impoundment		1.10/1.06	1.10/1.05	1.10/1.04	1.10/4.10	1.08/3.25	1.10/4.12	1.24/1.25	1.10/1.00	1.10/1.00
Mechanically Aerated Impoundment		1.00/0.84	1.00/1.00	1.00/0.76	1.00/0.91	1.00/0.99	1.00/0.81	1.00/0.93	1.00/1.00	--
Diffused Air System		1.00/1.00	1.00/1.00	1.00/1.00	1.00/0.99	1.00/1.00	1.00/0.99	1.01/1.00	1.00/0.99	--
Land Treatment (after tilling)		1.20/0.91	1.06/0.98	1.00/1.00	3.67/0.74	2.83/0.75	1.27/0.91	5.28/1.40	1.06/0.99	1.00/1.00
Oil Film Surface on Land Treatment Unit		0.92/1.31	0.92/1.28	0.92/1.25	3.93/1.09	5.68/1.06	3.98/1.09	1.08/0.77	0.92/1.00	0.92/1.03
Closed Landfill		1.20/1.01	1.18/1.01	1.16/1.00	1.14/1.01	1.11/1.01	1.14/1.02	1.18/1.02	1.18/0.99	1.20/1.00
Open Landfill		1.29/1.02	1.16/1.19	1.23/1.05	0.94/0.73	1.23/0.90	0.91/0.70	0.40/0.72	0.98/0.94	0.98/0.94
Wastepile		0.99/1.00	0.98/1.02	0.98/1.00	0.99/1.00	0.98/1.00	0.99/1.01	1.25/0.79	1.02/1.00	1.02/1.00
Fixed Roof Tank		*	*	*	0.82/0.53	0.81/0.53	0.82/0.50	0.90/0.89	*	*
Floating Roof Tank		*	*	*	1.00/1.01	0.96/1.01	0.98/1.00	0.95/1.01	*	*
Variable Vapor Space Tank		1.00/0.92	1.00/1.00	1.00/0.96	1.00/1.00	1.00/0.91	1.00/0.95	1.00/1.00	1.00/0.92	1.00/1.02
Storage Pile (Particulates)		0.88/1.00	--	--	-	--	--	--	--	--
Contaminated Area (Particulates)		0.98/0.98	--	--	--	--	--	--	--	--

*This type of tank is not typically used for materials with this high vapor pressure.

3.0 EXAMPLE APPLICATIONS

Two case studies have been selected to demonstrate the application of the alternative (scaling) air assessment screening methodology based on the technical aids presented in Appendices B through S. The first example involves a storage impoundment and the second a closed landfill.

3.1 Case Study A

Case Study A involves a storage impoundment located close to a small community. The closest resident lives 0.2 mile south of the unit. The impoundment has a surface area of 1 acre, a depth of 0.9 meter, and a typical storage time cycle of 1.2 days. Wind data from the nearest National Weather Service station indicate that northerly winds occur 10 percent of the time annually. Waste records for the unit indicate the frequent appearance of carbon tetrachloride. Limited waste analyses indicate that a 1,000-ppm concentration of this constituent in the impoundment is a reasonable assumption. The object of this example screening assessment is to estimate the ambient concentrations at the nearest residence. Following is a summary of this example application.

Step 1 - Obtain Source Characterization Information

The appropriate Emission Rate Estimation Worksheet for this case study is Table S-2 for storage impoundment units. The unit information provided above is sufficient to complete Column 2 for Lines 1-4 of the worksheet (see Exhibit 3-1) pursuant to Instruction A of the Worksheet (Table S-2).

Step 2 - Select Release Constituent Surrogates

Based on Figure 2-3, it is apparent that the Henry's Law Constant surrogate subset (Table B-1) is appropriate for a storage impoundment unit. Evaluation of Table B-3 indicates that the following surrogate is applicable to Case Study A:

EXHIBIT 3-1
TABLE S-2
EMISSION RATE ESTIMATION WORKSHEET - STORAGE IMPOUNDMENT EXAMPLE

Line	Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11
	Modeling Parameters	Instruction A: Input Unit-Specific Values	Instruction B: Select a Representative Case from Appendix D - Table D-1 (underline selected case)	Instruction C: Determine Surrogate-Specific Scaling Factors**							
				HVHB	HVMB	HVLB	MVHB	MVMB	MVLB	LVMB	VHVHB
1	Area*	1 acres	--	--	--	--	--	--	--	--	--
2	Depth*	0.9 m	1,2,3 or 4	____	0.57	____	____	____	____	____	____
3	Retention time*	1.2 days	5, 6, 7 or 8	____	4.1	____	____	____	____	____	____
4	Constituent concentration*	1000 ppm	--	--	--	--	--	--	--	--	--
	INSTRUCTION D: Complete Lines 5-6 and 8			SURROGATE-SPECIFIC VALUES							
5	Account for Area [unit-specific area/(Case 18 area = 0.4 acres)			____	2.5	____	____	____	____	____	____
6	Account for Unit-Specific Concentration [unit-specific conc./(Case 18 conc. = 1,000 ppm)]			____	1.0	____	____	____	____	____	____
7	Typical Surrogate-Specific Emission Rate (Case 18), 10^6 g/yr			34.0	39.24	3.25	38.10	38.40	1.97	38.74	39.24
8	Calculate Unit-Specific Emission Rate, 10^6 g/yr (multiply lines #2 x #3 x #5 x #6 x #7)			____	229.0	____	____	____	____	____	____

* Critical input values

** Scaling Factor determined for Lines 2 and 3 from Appendix D - Emission Rate Estimate from Table D-2 divided by Typical Emission Rate defined in Case 18 (see line 7).

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Constituent	Surrogate No.	Surrogate Code
• Carbon tetrachloride	3	HHLB

Step 3 - Calculate Emission Estimates

This step involves implementing Instructions B-D of the Worksheet (Table S-2). Instruction B involves selection of representative cases from Table D-1 which best match actual unit values in Column 2. A review of Table D-1 indicates that Case 1 (based on a depth of 0.9 meter) best estimates the depth of the example case (also a depth of 0.9 meters has been specified for Case Study A). Table D-1 also indicates that Case 5 (based on a retention cycle of 1 day) best represents the example case (a retention cycle of 1.2 days has been specified for Case Study A).

Implementation of Instruction C involves determination of surrogate-specific scaling factors. For this example this involved completion of Column 5 for lines 2 and 3 of the Worksheet (Table S-2). Emission rates for Cases 1 and 5, and a typical emission rate (Case 18) were obtained from Table D-2 as follows:

Case	Emission Rate (10^6g/yr)
	Carbon Tetrachloride
Case 1	22.5
Case 5	161.5
Case 18	39.2

Column 5 of the worksheet (for carbon tetrachloride) was completed via the following computations (Case 18 represents a typical emission rate for the source category of storage impoundment):

*Line 2:

$$\frac{\text{Case 1 Emission Rate (from Table D-2)}}{\text{Case 18 Emission Rate (from Line 7 of the Worksheet)}} = \frac{22.5}{39.2} = 0.57$$

*Line 3:

$$\frac{\text{Case 5 Emission Rate (from Table D-2)}}{\text{Case 18 Emission Rate (from Line 7 of the Worksheet)}} = \frac{161.5}{39.2} = 4.1$$

Implementation of Instruction D of the Worksheet (Table S-2) involves completion of Lines 5-6 and 8 as follows:

*Line 5:

$$\frac{\text{Unit-Specific Area (from Column 2 of the Worksheet)}}{\text{Case 18 Area (this value is identified in the Worksheet instructions for Line 5)}} = \frac{1.0}{0.4} = 2.5$$

*Line 6:

$$\frac{\text{Unit-Specific Concentration}}{\text{Case 18 Concentration}} = \frac{1,000}{1,000} = 1.0$$

*Line 8:

Emission Rate = Line 2 x Line 3 x Line 5 x Line 6 x Line 7
= 0.57 x 4.1 x 2.5 x 1.0 x 39.2
= 229.0 x 10^6g/yr
= 229.0 Mg/y

Step 4 - Calculate Concentration Estimates

This step involves use of the Concentration Estimation Worksheet (Table R-1). Application of the Worksheet involves implementation of Instructions A-D included in Table R-1. The example Concentration Estimation Worksheet for Case Study A is presented in Exhibit 3-2. Implementation of Instruction A involves input of the distance of the receptor from the downwind unit boundary for sectors of interest. Notice that the receptor distance of 0.2 mile (Column 2) corresponds with the south (downwind) sector. This is because the frequency of northerly winds obtained from the National Weather Service (as stated at the beginning of 3.1) represents the

EXHIBIT 3-2
TABLE R-1
CONCENTRATION ESTIMATION WORKSHEET - UNIT CATEGORY: CLOSED LANDFILL EXAMPLE

Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12	Col 13
				Instruction D: Compute Long-Term Concentration Estimates (μg/m³) Based on Equation 1* (select and circle appropriate surrogate subset, Henry's Law Constant or Raoult's Law or particle case)								
Downwind Sector	Instruction A: Input Distance to Receptors** (miles)	Instruction B: Determine Dispersion Factor (Figure R-1)	Instruction C: Assume Annual Downwind Frequency of 100% (percent)	MHLB or HVHB or particle case	HHLB or HVMB	LHMB or HVLB	MHMB or MVHB	HHMB or MVMB	LHHB or MVLB	MHHB or LVMB	HHHB or VHVHB	---- or VHVLB = Henry's Law Constant Surrogate = Raoult's Law Surrogate
N												
NNE												
NE												
ENE												
E												
ESE												
SE												
SSE												
S	0.2	6.4×10^{-5}	100		4600							
SSW												
SW												
WSW												
W												
WNW												
NW												
NNW												
Health Criteria (μg/m³) Based on RFI Guidance		Toxic Criteria			NA							
		Carcinogenic Criteria			0.03***							

* Equation 1 Long-Term Concentration Est. (μg/m³) = Col 3 x Col 4 x (unit/surrogate-specific Emission Rates, Mg/yr, based on Appendix S Worksheets) x (Conversion Factor = 3.17×10^{2}) / (Safety Factor = 10)
** Distance from downward unit boundary
*** Criterion for carbon tetrachloride
NA Not available
Mg/yr = 10^{6}g/yr

direction "from which the wind is flowing." This is standard meteorological terminology. Therefore, northerly winds affect receptors south of the unit.

Implementation of Instruction B involves determination of the appropriate dispersion factor for the downwind distance selected. The dispersion factor obtained from Figure R-1 for this example is 6.4×10^{-5} sec/m^3 (entered in Column 3 of the Concentration Estimation Worksheet). This value is applicable to a receptor 0.2 mile downwind from a 1-acre area source.

Implementation of Instruction C involves entering the downwind frequency for the sector of interest in Column 4 of the Worksheet. The downwind frequency (conservatively assumed to be 100 percent if Table R-1 dispersion factors are used) for a receptor located south of the unit is entered in Column 4 of the Worksheet.

Implementation of Instruction D involves computation of air concentrations based on Equation 1 of the Worksheet (Table R-1). The concentration estimate for carbon tetrachloride was calculated using Equation 1 of the Worksheet as follows:

- Worksheet estimate:

$$\begin{aligned}\text{Concentration } (\mu g/m^3) &= \text{Col. 3} \times \text{Col. 4} \times \text{Emission Rate} \times (\text{unit conversion} = 3.17 \times 10^2) \times (\text{Safety factor} = 10) \\ &= (6.4 \times 10^{-5}) \times (100) \times (229.0) \times (3.17 \times 10^2) \times (10) \\ &= 4600\ \mu g/m^3\end{aligned}$$

Step 5 - Compare Results to Health Criteria

Available health-based criteria from the RFI Guidance were entered into the Concentration Estimation Worksheet (see Exhibit 3-2). These results indicate that carbon tetrachloride concentrations at the nearest receptor significantly exceed the carcinogenic health-based criteria. Based on the expected carbon tetrachloride concentrations, this unit is a prime candidate for unit-specific emission rate and dispersion modeling to confirm the need for an RFI for the air media.

3.2 Case Study B

Case Study B involves a closed landfill of 7 acres with a waste-bed thickness of 25 feet and a cap thickness of 6 feet. Benzene is believed to be a primary constituent of the waste (approximately 10 percent). The closest resident lives 1 mile east of the unit. The prevailing winds (which occur 20 percent of the time annually, based on available facility data) are from the west (i.e., these winds will affect the downwind sector east of the unit). Following is a summary of the screening assessment for Case Study B.

Step 1 - Obtain Source Characterization Information

The appropriate Emission Rate Estimation Worksheet for Case Study B is Table S-8 for closed landfill units: The unit information provided is sufficient to complete Column 2 of the worksheet, with one exception (see Exhibit 3-3): the air porosity of the fixed waste is not known. Therefore, typical conditions [i.e., 25 percent as represented by Cases 14 and 22 (see Table J-1) will be assumed for this assessment].

Step 2 - Select Release Constituent Surrogates

Based on Figure 2-3, it is apparent that the Raoult's Law surrogate subset (Table B-2) is appropriate for a closed landfill unit. Evaluation of Table B-3 indicates that the following surrogate is applied to Case Study B:

Constituent	Surrogate No.	Surrogate Code
Benzene	1	HVHB

Step 3 - Calculate Emission Estimates

The calculational inputs for the Emission Rate Estimations Worksheets for Case Study B are presented in Exhibit 3-3 and 3-4. Scenario Case 1 (Exhibit 3-3) and Scenario Case 2 (Exhibit 3-4) were selected to bracket the actual waste-bed thickness for the example unit. Scenario Case 1 is associated with a waste-bed thickness of 15-feet and Case 2 with a 30-foot bed thickness. The actual waste-bed thickness is 25 feet. The resulting benzene emission rate estimates range from 46.4 x 10^6g/yr to 83.4 x 10^6g/yr.

EXHIBIT 3-3
TABLE S-8
EMISSION RATE ESTIMATION WORKSHEET - CLOSED LANDFILL EXAMPLE

Line	Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12
	Modeling Parameters	Instruction A: Input Unit-Specific Values	Instruction B: Select a Representative Case from Appendix J - Table J-1 (underline selected case)	Instruction C: Determine Surrogate-Specific Scaling Factors**								
				HVHB	HVMB	HVLB	MVHB	MVMB	MVLB	LVMB	VHVHB	VHVLB
1	Area*	7 acres	--	--	--	--	--	--	--	--	--	--
2	Waste-bed thickness*	25 ft	1,2,3 or 4	1.0	____	____	____	____	____	____	____	____
3	Cap thickness	6 ft	5, 6, 7 or 8	0.95	____	____	____	____	____	____	____	____
4	Constituent content of waste*	10 percent	9, 10, 11 or 12	1.0	____	____	____	____	____	____	____	____
5	Air porosity (fixed waste)	25 percent	13, 14, 15 or 16	1.0	____	____	____	____	____	____	____	____
	INSTRUCTION D: Complete Lines 6 and 8			SURROGATE-SPECIFIC VALUES								
6	Account for Area [unit-specific area/(Case 22 area = 3.5 acres)]			2.0	____	____	____	____	____	____	____	____
7	Typical Surrogate-Specific Emission Rate (Case 22), 10^6 g/yr			24.4	22.4	47.0	0.445	0.398	0.808	1.55E-05	119	264
8	Calculate Unit-Specific Emission Rate, 10^6 g/yr (multiply lines #2 x #3 x #4 x #5 x #6 x #7)			46.4	____	____	____	____	____	____	____	____

* Critical input values

** Scaling Factor determined for Lines 2-5 from Appendix J - Emission Rate Estimate from Table J-2 divided by Typical Emission Rate defined in Case 22 (see line 7).

EXHIBIT 3-4
TABLE S-8
EMISSION RATE ESTIMATION WORKSHEET - CLOSED LANDFILL EXAMPLE

Line	Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12
	Modeling Parameters*	Instruction A: Input Unit-Specific Values	Instruction B: Select a Representative Case from Appendix F - Table F-1 (underline selected case)	Instruction C: Determine Surrogate-Specific Scaling Factors**								
				HVHB	HVMB	HVLB	MVHB	MVMB	MVLB	LVMB	VHVHB	VHVLB
1	Area*	7 acres	--	--	--	--	--	--	--	--	--	--
2	Waste-bed thickness*	25 ft	1,2,3 or 4	1.8	___	___	___	___	___	___	___	___
3	Cap thickness	6 ft	5, 6, 7 or 8	0.95	___	___	___	___	___	___	___	___
4	Constituent content of waste*	10 percent	9, 10, 11 or 12	1.0	___	___	___	___	___	___	___	___
5	Air porosity (fixed waste)	25 percent	13, 14, 15 or 16	1.0	___	___	___	___	___	___	___	___
	INSTRUCTION D: Complete Lines 6 and 8			SURROGATE-SPECIFIC VALUES								
6	Account for Area [unit-specific area/(Case 22 area = 3.5 acres)]			2.0	___	___	___	___	___	___	___	___
7	Typical Surrogate-Specific Emission Rate (Case 22), 10^6 g/yr			24.4	22.4	47.0	0.445	0.398	0.808	1.55E-05	119	264
8	Calculate Unit-Specific Emission Rate, 10^6 g/yr (multiply lines #2 x #3 x #4 x #5 x #6 x #7)			83.4	___	___	___	___	___	___	___	___

* Critical input values

** Scaling Factor determined for Lines 2-5 from Appendix J - Emission Rate Estimate from Table J-2 divided by Typical Emission Rate defined in Case 22 (see line 7).

Step 4 - Calculate Concentration Estimates

The example Concentration Estimation Worksheets for Case Study B are presented in Exhibits 3-5 (Scenario Case 1) and 3-6 (Scenario Case 2). The resulting benzene concentration at the nearest receptor is estimated to range from 69 $\mu g/m^3$ to 124 $\mu g/m^3$.

Step 5 - Compare Results to Health Criteria

A review of results presented in Exhibits 3-5 and 3-6 indicates that the estimated benzene concentrations of 69 $\mu g/m^3$ to 124 $\mu g/m^3$ are approximately 1000 times the carcinogenic criterion of 0.1 $\mu g/m^3$. A toxic criterion is not available for benzene. Based on the results presented in Exhibits 3-5 and 3-6, this unit is a prime candidate for an air release RFI.

EXHIBIT 3-5
TABLE R-1
CONCENTRATION ESTIMATION WORKSHEET - UNIT CATEGORY: CLOSED LANDFILL EXAMPLE (Scenario Case 1)

Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12	Col 13	
				Instruction D: Compute Long-Term Concentration Estimates (μg/m³) Based on Equation 1* (select and circle appropriate surrogate subset, Henry's Law Constant or Raoult's Law or particle case)									
Downwind Sector	Instruction A: Input Distance to Receptors** (miles)	Instruction B: Determine Dispersion Factor (Figure R-1)	Instruction C: Assume Annual Downwind Frequency of 100% (percent)	MHLB or HVHB or particle case	HHLB or HVMB	LHMB or HVLB	MHMB or MVHB	HHMB or MVMB	LHHB or MVLB	MHHB or LVMB	HHHB or VHVHB	---- or VHVLB	= Henry's Law Constant Surrogate = Raoult's Law Surrogate
N													
NNE													
NE													
ENE													
E	1.0	4.7×10^{-6}	100	69									
ESE													
SE													
SSE													
S													
SSW													
SW													
WSW													
W													
WNW													
NW													
NNW													
Health Criteria (μg/m³) Based on RFI Guidance		Toxic Criteria		NA									
		Carcinogenic Criteria		0.1***									

* Equation 1 Long-Term Concentration Est. (μg/m³) = Col 3 x Col 4 x (unit/surrogate-specific Emission Rates, Mg/yr, based on Appendix S Worksheets) x (Conversion Factor = 3.17×10^{2}) x (Safety Factor = 10)

** Distance from downward unit boundary

*** Criterion for benzene

NA Not available

Mg/yr = 10^{6}g/yr

EXHIBIT 3-6
TABLE R-1
CONCENTRATION ESTIMATION WORKSHEET - UNIT CATEGORY: CLOSED LANDFILL EXAMPLE (Scenario Case 2)

Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12	Col 13
				Instruction D: Compute Long-Term Concentration Estimates (μg/m³) Based on Equation 1* (select and circle appropriate surrogate subset, Henry's Law Constant or Raoult's Law or particle case)								
Downwind Sector	Instruction A: Input Distance to Receptors** (miles)	Instruction B: Determine Dispersion Factor (Figure R-1)	Instruction C: Assume Annual Downwind Frequency of 100% (percent)	MHLB or HVHB or particle case	HHLB or HVMB	LHMB or HVLB	MHMB or MVHB	HHMB or MVMB	LHHB or MVLB	MHHB or LVMB	HHHB or VHVHB	---- or VHVLB = Henry's Law Constant Surrogate = Raoult's Law Surrogate
N												
NNE												
NE												
ENE												
E	1.0	4.7×10^{6}	100	124								
ESE												
SE												
SSE												
S												
SSW												
SW												
WSW												
W												
WNW												
NW												
NNW												
Health Criteria (μg/m³) Based on RFI Guidance		Toxic Criteria		NA								
		Carcinogenic Criteria		0.1***								

* Equation 1 Long-Term Concentration Est (μg/m³) = Col 3 x Col 4 x (unit/surrogate specific Emission Rates, Mg/yr, based on Appendix S Worksheets) x (Conversion Factor = 3.17×10^{-5}) x (Safety Factor = 10)

** Distance from downward unit boundary

*** Criterion for benzene

NA Not available

Mg/yr = 10^{6}g/yr

4.0 REFERENCES

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U.S. EPA, June 1974. Development of Emission Factors for Fugitive Dust Sources, Research Triangle Park, NC, 27711.

U.S. EPA, March 1978. Fugitive Emissions from Integrated Iron and Steel Plants, EPA 600/2-78-050, Washington, D.C.

U.S. EPA, July 1988. Guidelines on Air Quality Models (Revised), EPA-450/2-78-027R, Office of Air Quality Planning and Standards, Research Triangle Park, NC 27711.

U.S. EPA. December 1987. Hazardous Waste Treatment Storage and Disposal Facilities (TSDF) Air Emission Models. Office of Air Quality Planning and Standards. Research Triangle Park, NC 27711 (CHEMDAT6).

U.S. EPA, 1989. RCRA Facility Investigation (RFI) Guidance. Office of Solid Waste, Washington, D.C. 20460.

Turner, D.B. 1969. Workbook of Atmospheric Dispersion Estimates. Public Health Service, Cincinnati, OH.

Appendix A

Background Information

A.0 BACKGROUND INFORMATION

The air release screening assessment methodology has been developed based on use of available air emissions models applicable to facilities for treatment, storage, and disposal of hazardous waste, and on results of atmospheric dispersion modeling. The emission models were used to calculate emission rates for a wide range of source scenarios. (An emission rate is defined as the source release rate for the air pathway in terms of mass per unit of time.) These modeling results have been summarized in this document so that they can be easily used by Environmental Protection Agency (EPA) Regional and State Agency staff to estimate emission rates for facility-specific and unit-specific applications. These source-specific emission rates can be used in conjunction with dispersion modeling results, representative of typical annual conditions, to estimate long-term ambient concentrations at locations of interest. (Ambient concentrations are defined as the concentrations of the released constituent downwind from the source.) The emission rate and atmospheric dispersion modeling approaches used to develop the screening methodology are discussed in the subsections that follow.

A.1 Emission Rate Models

The air release screening assessment methodology has been based primarily on application of air emission models (available on a diskette for use on a microcomputer) developed by EPA's Office of Air Quality Planning and Standards (OAQPS) to estimate organic releases for hazardous waste treatment, storage, and disposal facilities (TSDFs) (U.S. EPA, December 1987). Computer-compatible air emission models (referred to as CHEMDAT6 models) are available for the following sources:

- Surface impoundments, which for modeling purposes include quiescent impoundments, aerated impoundments, and open-top tanks
  - Disposal impoundments
  - Storage impoundments
  - Oil films on storage impoundments
  - Aerated impoundments

- Land treatment
  - Soil emissions subsequent to waste tilling
  - Oil film surfaces
- Closed landfills
- Open landfills
- Wastepiles

Since the results presented in this document are based on the December 1987 version of CHEMDAT6, subsequent modifications to any of these models may require revisions to this screening methodology

The available models for CHEMDAT6 provide a basis to estimate emissions for numerous unit categories (e.g., surface impoundments, landfills) as previously listed. Therefore, the CHEMDAT6 models will be applicable to a wide range of air release screening assessments. CHEMDAT6 (December 1987 versions) does not, however, include models for the following sources:

- Land treatment - waste application
- Fixation pits
- Container loading
- Container storage
- Container cleaning
- Stationary tank loading
- Stationary tank storage
- Fugitive emissions
- Vacuum truck loading

However, guidance for estimating organic emissions from these sources is available from OAQPS (U.S. EPA, December 1987).

In addition to the CHEMDAT6 model, emission equations from EPA's AP-42, "Compilation of Air Pollutant Emission Factors" and "Fugitive Emissions from Integrated Iron and Steel Plants" have been used for estimating organic emissions from storage tanks and particulate matter emissions that are less than 10 microns in diameter from storage piles and exposed areas which result from wind erosion and activities on storage piles.

A.2 Source Scenarios

A wide range of source scenarios were evaluated as a basis for developing the air release assessment methodology. This involved identification of a limited set of surrogates to represent the numerous individual potential air release constituents of concern. This also involved evaluating of the sensitivity of the input parameters used by the CHEMDAT6 air emission models and the AP-42 emission equation input parameters.

A.2.1 Release Constituent Surrogates

A limited set of surrogates was required to simplify the air release assessment methodology since the list of potential air release constituents included in the RFI Guidance (U.S. EPA, 1988) is extensive. The set of surrogates selected for this application was the same list developed by OAQPS for assessment of organic emissions from TSDFs (see Appendix B).

Two subsets of surrogates are presented in Appendix B. The first subset is applicable to air emission modeling applications based on the use of the Henry's Law Constant (Table B-1) and the second subset is based on use of Raoult's Law (Table B-2). Raoult's Law accurately predicts the behavior of most concentrated mixtures of water and organic solvents (i.e., solutions over 10 percent solute). According to Raoult's Law, the rate of volatilization of each chemical in a mixture is proportional to the product of its concentration in the mixture and its vapor pressure. Therefore, Raoult's Law can be used to characterize potential for volatilization. This is especially useful when the unit of concern entails container storage, tank storage, or treatment of concentrated waste streams.

The Henry's Law Constant is the ratio of the vapor pressure of a constituent to its aqueous solubility (at equilibrium). This constant can be used to assess the relative ease with which the compound may vaporize from the aqueous solution and will be most useful when the unit being assessed is a surface impoundment or tank containing dilute wastewaters. The potential for significant vaporization increases as the value for the Henry's Law Constant increases; when it is greater than 10E-3, rapid volatilization will generally occur.

The surrogates presented in Appendix B span the range from very high volatility to low volatility (frequently classified as semi-volatiles). Biodegradation potential has also been accounted for in the surrogate specifications. Therefore, a cross-reference of constituents has also been provided in Appendix B (Table B-3). This listing provides the basis for the identification of the appropriate surrogate for individual air release constituents of interest. Instructions for use of Appendix B data are provided in Section 2.

A.2.2 Sensitivity Analyses

Sensitivity analyses of the input parameters used by the CHEMDAT6 air emission models emission rate relative to output were evaluated to determine the feasibility of developing a source characterization index. The object of the source characterization index was to define a simple relationship between the primary source description parameters and the emission rate of the release. This evaluation was accomplished by modeling a series of source scenario cases for each unit category (i.e., categories such as surface impoundments and landfills). Each of these source scenario cases represents long-term (i.e., annual) emission conditions. A base case representative of typical source conditions was defined for each unit category. These typical conditions were specified based on TSDF survey results and on guidance presented in the OAQPS air emissions modeling report (U.S. EPA, December 1987). This base case provided a standard for comparison to results of parametric analyses. The parametric analyses consisted of varying (one at a time) the input values for the most sensitive modeling parameters. These input parameter values were varied over a range of expected source conditions. In addition to the parametric analyses and the typical (base-case) scenario, a reasonable best-case (minimum emission rate) and a reasonable worst-case (maximum emission rate) source scenario were also modeled. The most sensitive modeling parameters and their associated range of values were determined by considering model sensitivity results and TSDF source survey information presented in the OAQPS air emission modeling report (U.S.EPA, December 1987), as well as other judgmental factors. A similar sensitivity analysis was performed for the three tank types.

A summary of the air emissions modeling parameters, input values, and modeling results (emission rates) is presented in Appendices C through Q. Evaluation of these results indicates that emission rates are highly dependent on numerous sensitive source parameters. Therefore, these complex relationships are not conducive to development of a source characterization index (i.e., defining a simple relationship between the primary source description parameters and the emission rate of the release). However, the modeling results presented in Appendices C through Q provide data which can be interpolated to estimate unit-specific emission rates with minimal guidance. The methodology for application of these data is discussed in Section 2.

A.3 Atmospheric Dispersion Conditions

Atmospheric dispersion conditions affect the downwind dilution of emissions from a source. Available EPA dispersion models can be used to account for site specific meteorological and source conditions. For this screening assessment, modeling results are presented which represent typical dispersion conditions (neutral stability and 10-mph winds) in the United States.

Dispersion modeling results to be used for the screening assessment (assuming flat terrain) are presented in Appendix R (Figure R-1) and are applicable to ground-level sources with non-buoyant releases (this assumption is valid for surface impoundments, land treatment units, landfills, waste piles, tanks, and exposed areas). These results are presented in terms of dispersion factors. Dispersion factors can be considered as the ratio of the ambient concentration to the source emission rate. Therefore, dispersion factors facilitate the calculation of ambient concentrations if emission rate estimates are available.

The dispersion factors presented in Figure R-1 were developed from similar dispersion graphs presented in a standard technical reference (Turner, 1969). These dispersion factors are applicable to long-term (e.g., annual) conditions. It has been assumed that dispersion factors (and, thus also ambient concentrations) decrease as a function of downwind distance but are uniform in the crosswind direction within a 22.5 degree sector (22.5 degree sectors correspond with major compass directions such as N, NNW, NW, etc.). The dispersion factors presented in Figure R-1 also account for the initial plume size, which corresponds to the surface area of the

source (Turner, 1969). Results presented in Figure R-1 are expected to be similar to results from the EPA-approved Industrial Source Complex dispersion model.

Appendix B

Release Constituent Surrogate Data

TABLE B-1
SURROGATE PROPERTIES - HENRY'S LAW CONSTANT SUBSET

Code	No.	Characteristics	Henry's Law* Constant 298°K
MHLB	6	medium Henry's Law, low biodegradation	2.22E-05
HHLB	3	high Henry's Law, low biodegradation	3.00E-02
LHMB	8, 9	low Henry's Law, medium biodegradation	1.58E-07
MHMB	5	medium Henry's Law, medium biodegradation	4.08E-05
HHMB	2	high Henry's Law, medium biodegradation	1.18E-03
LHHB	7	low Henry's Law, high biodegradation	1.58E-07
MHHB	4	medium Henry's Law, high biodegradation	6.80E-05
HHHB	1	high Henry's Law, high biodegradation	5.38E-03

*Key: low Henry's Law Constant $<1.0E-05$ atm-m^3/g mol
medium Henry's Law Constant 1.0E-05 - 1.0E-3
high Henry's Law Constant $>1.0E-03$

TABLE B-2
SURROGATE PROPERTIES - RAOULT'S LAW SUBSET

Code	No.	Characteristics	Vapor Pressure (25°C)
HVHB	1	high volatility, high biodegradation	206
HVMB	2	high volatility, medium biodegradation	182
HVLB	3	high volatility, low biodegradation	256
MVHB	4	medium volatility, high biodegradation	2.62
MVMB	5	medium volatility, medium biodegradation	2.02
MVLB	6	medium volatility, low biodegradation	2.91
LVMB	7, 8, 9	low volatility, medium biodegradation	0.0001
VHVHB	10, 11	very high volatility, high biodegradation	1890
VHVLB	12	very high volatility, low biodegradation	2030

*Key: low volatility, <1.0E-05 atm
medium volatility, 1.0E-05 - 1.0E-3
high volatility, 1.0E-03 - 1.0
very high volatility, >1.0

TABLE B-3
LISTING OF CONSTITUENT-SPECIFIC SURROGATES

Constituent	CAS No.	Henry's Law Constant Surrogate Code	Raoult's Law Surrogate Code
Acrylamide	79-06-1	7	4
Acrylonitrile	107-13-1	4	1
Aldicarb	116-06-3	8	9
Aldrin	309-00-2	3	7
Aniline	62-53-3	8	5
Arsenic	7440-38-2	0	0
Benz(a)anthracene	56-55-3	9	7
Benzene	71-43-2	1	1
Benzo(a)pyrene	50-32-8	9	8
Beryllium	7440-41-7	0	0
Bis(2-chloroethyl)ether	111-44-4	5	5
Bromodichloromethane	75-27-4	3	7
Cadmium	7440-43-9	0	0
Carbon tetrachloride	56-23-5	3	3
Chlordane	57-74-9	6	7
1-Chloro-2, 3-epoxypropane (Epichlorohydrin)	106-89-8	6	3
Chloroform	67-66-3	3	3
Chromium (hexavalent)	7440-47-3	0	0
DDT	50-29-3	3	7
Dibenz(a,h) anthracene	53-70-3	9	7
1,2-Dibromo-3-Chloropropane (DBCP)	96-12-8	6	6
1,2-Dibromoethane	106-93-4	3	3
1,2-Dichloroethane	107-06-2	3	3
1,1-Dichloroethylene	75-35-4	3	3
Dichloromethane (Methylene chloride)	75-09-2	1	1

TABLE B-3
LISTING OF CONSTITUENT-SPECIFIC SURROGATES (Continued)

Constituent	CAS No.	Henry's Law Constant Surrogate Code	Raoult's Law Surrogate Code
2,4-Dichlorophenol	120-83-2	8	5
2,4-Dinitrophenol	51-28-5	9	3
2,4-Dinitrotoluene	121-14-2	9	6
1,4-Dioxane	123-91-1	6	3
1,2-Diphenylhydrazine	122-66-7	9	7
Endosulfan	115-29-7	9	7
Ehtylene oxide	75-21-8	4	10
Heptachlor	76-44-8	3	7
Hexachlorobenzene	118-74-1	6	7
Hexachlorobutadiene	87-68-3	3	6
Hexachloroethane	67-72-1	9	6
Hydrazine	302-01-2	9	3
Isobutyl alcohol	78-83-1	7	4
Lindane (gamma-Hexachlorocyclohexane)	58-89-9	9	7
3-Methyl-cholanthrene	56-49-5	6	7
4,4-Methylene-bis-(2-chloroaniline)	101-14-4	3	6
Methyl parathion	298-00-0	6	6
Nickel	1440-02-0	0	0
Nickel (refinery dust)	7440-02-0	0	0
Nickel subsulfide	12035-72-2	0	0
2-Nitropropane	79-46-9	6	3
N-Nitroso-N-methyl urea	684-93-5	5	9
N-Nitroso-pyrrolidine	930-55-2	2	2
Pentachlorobenzene	608-93-5	3	6
Pentachlorophenol	87-86-5	9	7

TABLE B-3
LISTING OF CONSTITUENT-SPECIFIC SURROGATES (Continued)

Constituent	CAS No.	Henry's Law Constant Surrogate Code	Raoult's Law Surrogate Code
Perchloroethylene (Tetrachloroethylene)	127-18-4	3	3
Styrene	100-42-5	3	6
1,2,4,5-Tetrachlorobenzene	95-94-3	3	6
1,1,2,2-Tetrachloroethane	79-34-5	6	6
2,3,4,6-Tetrachlorophenol	58-90-2	9	6
Tetraethyl lead	78-00-2	3	6
Thiourea	62-56-6	6	3
Toxaphene	8001-35-2	3	6
1,1,2-Trichloroethane	79-00-5	6	3
Trichloroethylene	79-01-6	3	3
2,4,5-Trichlorophenol	95-95-4	6	6
2,4,6-Trichlorophenol	88-06-2	6	6

Appendix C

Emission Rate Estimates
Disposal Impoundments
(Quiescent Surfaces)

TABLE C-1
EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - DISPOSAL IMPOUNDMENT*

Modeling Parameters	CASE NUMBERS																		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17**	18***	19****
Area (acres)	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2
Depth (m)	0.9	1.8	3.6	5.0	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	0.9	1.8	3.6
Turnovers (per yr)	2	2	2	2	0.5	1	2	3	2	2	2	2	2	2	2	2	1	2	3
Constituent concentration (ppm)	1000	1000	1000	1000	1000	1000	1000	1000	10	1000	2000	4000	1000	1000	1000	1000	10	1000	4000
Air temperature (°C)	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
Wind speed (mph)	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1	1	1	5	10	70	1	1	1

* Input assumptions:
- Active biomass = 0.0 g/l
- Biomass solids in = 0.0 m^3/sec
- Submerged air flow = 0.0 m^3/sec

** Reasonable Best Case (minimum) Emissions (assuming typical source area)
*** Typical Emission Conditions (assuming typical source area)
**** Reasonable Worst Case (maximum) Emissions (assuming typical source area)

Note: If actual input values vary significantly from the above scenarios it is recommended that CHEMDAT6 be used to calculate emission estimates directly

TABLE C-2
EMISSION RATE ESTIMATES (10^6 g/yr) - DISPOSAL IMPOUNDMENT

Henry's Law Constant Surrogate	(Case 1)	(Case 2)	(Case 3)	(Case 4)	(Case 5)	(Case 6)	(Case 7)	(Case 8)
MHLB	16.2	32.4	64 8	89 9	8.1	16.2	32 4	48 6
HHLB	16 2	32.4	64.8	90.0	8.1	16 2	32 4	48 6
LHMB	11.0	14.1	16 1	16 7	7.3	11.0	14.1	15 4
MHMB	16.2	32 4	64.8	90.0	8 1	16.2	32.4	48 6
HHMB	16 2	32.4	64 8	90.0	8.1	16 2	32 4	48 6
LHHB	8 0	9.4	10.1	10.4	6 0	8 0	9 4	9.9
MHHB	16.2	32.4	64.8	90 0	8 1	16 2	32 4	48 6
HHHB	16 2	32.4	64 8	90.0	8.1	16 2	32.4	48 6

Henry's Law Constant Surrogate	(Case 9)	(Case 10)	(Case 11)	(Case 12)	1 Year (Case 13)	5 Years (Case 14)	10 Years (Case 15)	70 Years (Case 16)
MHLB	0.3	32.4	64 8	129 6	32.4	32.4	32.4	32 4
HHLB	0.3	32.4	64.8	129 6	32.4	32.4	32 4	32 4
LHMB	0.1	14.1	28.2	56 4	14 1	14.1	14.1	14 1
MHMB	0.3	32.4	64.8	129.6	32.4	32 4	32.4	32.4
HHMA	0.3	32.4	64 8	129.6	32 4	32.4	32 4	32 4
LHHB	0.1	9.4	18 7	37.5	9.4	9 4	9.4	9 4
MHHB	0 3	32 4	64 8	129 6	32.4	32 4	32.4	32 4
HHHB	0 3	32 4	64.8	129 6	32 4	32 4	32 4	32 4

Henry's Law Constant Surrogate	(Case 17)	(Case 18)	(Case 19)					
MHLB	0 1	32 4	388 4					
HHLB	0 1	32 4	388 8					
LHMB	0 1	14 1	67 5					
MHMB	0 1	32.4	388 8					
HHMB	0.1	32 4	388 8					
LHHB	0 1	9 4	41 6					
MHHB	0 1	32 4	388 8					
HHHB	0 1	32 4	388 8					

Appendix D

Emission Rate Estimates
Storage Impoundments/Open Tanks
(Quiescent Surfaces)

TABLE D-1
EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - STORAGE IMPOUNDMENT*

Modeling Parameters	CASE NUMBERS																		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17**	18***	19****
Area (acres)	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Depth (m)	0.9	1.8	3.6	5.0	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	0.9	1.8	5.0
Retention time (days)	20	20	20	20	1	20	50	550	20	20	20	20	20	20	20	20	550	20	1
Constituent concentration (ppm)	1000	1000	1000	1000	1000	1000	1000	1000	10	1000	2000	4000	1000	1000	1000	1000	10	1000	4000
Air temperature (°C)	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
Wind speed (mph)	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1	1	1	5	10	70	1	1	1

* Input assumptions:
- Active biomass = 0.0 g/l
- Biomass solids in = 0.0 m³/sec

** Reasonable Best Case (minimum) Emissions (assuming typical source area)

*** Typical Emission Conditions (assuming typical source area)

**** Reasonable Worst Case (maximum) Emissions (assuming typical source area)

Note: If actual input values vary significantly from the above scenarios it is recommended that CHEMDAT6 be used to calculate emission estimates directly

TABLE D-2
EMISSION RATE ESTIMATES (10^6 g/yr) - STORAGE IMPOUNDMENTS

Henry's Law Constant Surrogate	(Case 1)	(Case 2)	(Case 3)	(Case 4)	(Case 5)	(Case 6)	(Case 7)	(Case 8)
MHLB	20.7	34.0	57 9	69.4	99.4	34.0	16 7	1.8
HHLB	22.5	39.2	74.1	94.1	161.5	39.2	17.9	1.8
LHMB	3.1	3 2	3 3	3 4	3 9	3 2	3.0	1 2
MHMB	22.0	38.1	69 0	86 0	143 8	38.1	17.7	1.8
HHMB	22.3	38.4	72.2	90.9	148.7	38 4	17.7	1.8
LHHB	1.9	2.0	2.1	2.1	2.0	2.0	1.9	1.0
MHHB	22.2	38.7	71.2	89.3	153.6	38 7	17 8	1 8
HHHB	22.5	39 2	74 1	94.1	161.5	39 2	17 9	1 8

Henry's Law Constant Surrogate	(Case 9)	(Case 10)	(Case 11)	(Case 12)	1 Year (Case 13)	5 Years (Case 14)	10 Years (Case 15)	70 Years (Case 16)
MHLB	0.3	34.0	68.0	136.1	34.0	34 0	34.0	34 0
HHLB	0.4	39.2	78.5	156 9	39.2	39.2	39 2	39 2
LHMB	0.03	3.2	6 5	13 0	3 2	3 2	3 2	3 2
MHMB	0.4	38.1	76.2	152.4	38.1	38 1	38.1	38.1
HHMB	0.4	38.4	76.8	153.6	38.4	38.4	38.4	38.4
LHHB	0.02	2.0	3.9	7.9	2.0	2.0	2.0	2 0
MHHB	0.4	38.7	77.5	155.0	38 7	38.7	38.7	38.7
HHHB	0.4	39.2	78.5	156 9	39.2	39.2	39 2	39 2

Henry's Law Constant Surrogate	(Case 17)	(Case 18)	(Case 19)					
MHLB	0 01	34.02	536.88					
HHLB	0.01	39 24	1084 72					
LHMB	0 01	3 25	10 96					
MHMB	0 01	38 10	854 63					
HHMB	0 01	38 40	986 11					
LHHB	0 01	1 97	10 96					
MHHB	0 01	38 74	942 28					
HHHB	0 01	39 24	1084 72					

Appendix E

Emission Rate Estimates
Oil Films on Storage Impoundments

TABLE E-1
EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - OIL FILM ON STORAGE IMPOUNDMENT*

Modeling Parameters	CASE NUMBERS																		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17**	18***	19****
Area (acres)	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Depth of oil film (m)	7.2E-04	7.2E-03	7.2E-02	7.2E-01	7.2E-02	7.2E-02	7.2E-02	7.2E-02	7.2E-02	7.2E-02	7.2E-02	7.2E-02	7.2E-02	7.2E-02	7.2E-02	7.2E-02	7.2E-04	7.2E-02	7.2E-01
Retention time (days)	20	20	20	20	1	20	50	365	20	20	20	20	20	20	20	20	365	20	1
Constituent concentration in oil (ppm)	200	200	200	200	200	200	200	200	100	200	1000	5000	200	200	200	200	100	200	5000
Air temperature (°C)	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
Wind speed (mph)	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1	1	1	5	10	70	1	1	1

* Input assumptions:
- Oil (fraction of waste) = 1.0
- Molecular weight of oil = 282
- Density of oil = 1.0

** Reasonable Best Case (minimum) Emissions (assuming typical source area)
*** Typical Emission Conditions (assuming typical source area)
**** Reasonable Worst Case (maximum) Emissions (assuming typical source area)

Note: If actual input values vary significantly from the above scenarios it is recommended that CHEMDAT6 be used to calculate emission estimates directly

TABLE E-2
EMISSION RATE ESTIMATES (10^6 g/yr) - OIL FILMS ON STORAGE IMPOUNDMENTS

Raoult's Law Surrogate	(Case 1)	(Case 2)	(Case 3)	(Case 4)	(Case 5)	(Case 6)	(Case 7)	(Case 8)
HVHB	3.94E-03	0.039	0.394	3.942	7.884	0.394	0.158	0.022
HVMB	3.94E-03	0.039	0.394	3.942	7.884	0.394	0.158	0.022
HVLB	3.94E-03	0.039	0.394	3.942	7.884	0.394	0.158	0.022
MVHB	3.94E-03	0.039	0.394	1.851	2.115	0.394	0.158	0.022
MVMB	3.94E-03	0.039	0.389	1.388	1.517	0.389	0.158	0.022
MVLB	3.94E-03	0.039	0.394	1.868	2.137	0.394	0.158	0.022
LVMB	1.08E-04	1.10E-04	1.10E-04	1.06E-04	1.02E-04	1.10E-04	1.10E-04	1.08E-04
VHVHB	3.94E-03	0.039	0.394	3.942	7.884	0.394	0.158	0.022
VHVLB	3.94E-03	0.039	0.394	3.942	7.884	0.394	0.158	0.022
Raoult's Law Surrogate	**(Case 9)**	**(Case 10)**	**(Case 11)**	**(Case 12)**	**1 Year (Case 13)**	**5 Years (Case 14)**	**10 Years (Case 15)**	**70 Years (Case 16)**
HVHB	0.197	0.394	1.971	9.855	0.394	0.394	0.394	0.394
HVMB	0.197	0.394	1.971	9.855	0.394	0.394	0.394	0.394
HVLB	0.197	0.394	1.971	9.855	0.394	0.394	0.394	0.394
MVHB	0.197	0.394	1.968	9.838	0.394	0.394	0.394	0.394
MVMB	0.195	0.389	1.945	9.727	0.389	0.389	0.389	0.389
MVLB	0.197	0.394	1.968	9.839	0.394	0.394	0.394	0.394
LVMB	5.50E-05	1.10E-04	5.50E-04	2.75E-03	1.10E-04	1.10E-04	1.10E-04	1.10E-04
VHVHB	0.197	0.394	1.971	9.855	0.394	0.394	0.394	0.394
VHVLB	0.197	0.394	1.971	9.855	0.394	0.394	0.394	0.394
Raoult's Law Surrogate	**(Case 17)**	**(Case 18)**	**(Case 19)**					
HVHB	1.08E-04	0.394	1863.51					
HVMB	1.08E-04	0.394	1886.53					
HVLB	1.08E-04	0.394	1904.63					
MVHB	1.08E-04	0.394	60.60					
MVMB	1.08E-04	0.394	41.68					
MVLB	1.08E-04	0.394	61.35					
LVMB	4.25E-05	1.10E-04	1.97E-03					
VHVHB	1.08E-04	0.394	1971.00					
VHVLB	1.08E-04	0.394	1971.00					

Appendix F

Emission Rate Estimates
Mechanically Aerated Impoundments

TABLE F-1
EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - MECHANICALLY AERATED IMPOUNDMENT*

Modeling Parameters	CASE NUMBERS																						
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21**	22***	23****
Area (acres)	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Depth (m)	0.9	1.8	3.6	5.0	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	0.9	1.8	5.0
Retention time (days)	10	10	10	10	3	10	15	20	10	10	10	10	10	10	10	10	10	10	10	10	20	10	3
Constituent concentration (ppm)	1000	1000	1000	1000	1000	1000	1000	1000	10	1000	2000	4000	1000	1000	1000	1000	1000	1000	1000	1000	10	1000	4000
Fraction agitated	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.17	0.24	0.52	0.87	0.24	0.24	0.24	0.24	0.17	0.24	0.87
Air temperature (°C)	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
Wind speed (mph)	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	5	10	70	1	1	1

* Input assumptions:
- Active biomass = 0.0 g/l
- Biomass solids in = 0.0 m³/sec
- Submerged air flow = 0.0 m³/sec
- Number of impellers = 1
- Oxygen transfer correction factor = 0.83
- Impeller diameter = 61 cm
- Impeller speed = 126 rad/sec

** Reasonable Best Case (minimum) Emissions (assuming typical source area)
*** Typical Emission Conditions (assuming typical source area)
**** Reasonable Worst Case (maximum) Emissions (assuming typical source area)

Note: If actual input values vary significantly from the above scenarios it is recommended that CHEMDAT6 be used to calculate emission estimates directly

TABLE F-2
EMISSION RATE ESTIMATES (10^6 g/yr) - MECHANICALLY AERATED IMPOUNDMENTS

Henry's Law Constant Surrogate	(Case 1)	(Case 2)	(Case 3)	(Case 4)	(Case 5)	(Case 6)	(Case 7)	(Case 8)
MHLB	47.2	90.6	168 1	220.8	253 9	90 6	62 1	47.2
HHLB	49.2	98 4	196 5	272 6	326 9	98 4	65 6	49 2
LHMB	11.0	12 3	13.2	13.4	13 5	12 3	11.6	11 0
MHMB	48.3	94 7	182 6	246 5	289 4	94 7	64.0	48 3
HHMB	49 2	98.3	195 8	271.2	324 9	98 3	65 6	49.2
LHHB	7.9	8 5	8.9	9 0	9 1	8 5	8 2	7 9
MHHB	48.6	95.9	187.0	254.6	300.9	95 9	64.5	48.6
HHHB	49 2	98 4	186 4	272 3	326 6	98 4	65 6	49 2

Henry's Law Constant Surrogate	(Case 9)	(Case 10)	(Case 11)	(Case 12)	(Case 13)	(Case 14)	(Case 15)	(Case 16)
MHLB	0 91	90 6	181.2	362 4	86 6	90 6	95 4	97 0
HHLB	0.98	98.4	196 9	393 8	98 4	98 4	98.5	98 6
LHMB	0.12	12.3	24 7	49.4	8 9	12 3	25 5	40 2
MHMB	0 95	94.7	189.5	379 0	92 6	94 7	97 1	97 9
HHMB	0 98	98.3	196 5	393.0	98 0	98 3	98 5	98 5
LHHB	0.085	8.5	17.1	34 2	6.0	8 5	18 8	31 3
MHHB	0 96	95.9	191 9	383 8	94 4	95 9	97 6	98 1
HHHB	0 98	98.4	196 8	393 6	98 3	98 4	98 5	98 6

Henry's Law Constant Surrogate	1 Year (Case 17)	5 Years (Case 18)	10 Years (Case 19)	70 Years (Case 20)	(Case 21)	(Case 22)	(Case 23)	
MHLB	90 6	90 6	90 6	90 6	0 24	90 6	3,169 2	
HHLB	98.4	98 4	98 4	98 4	0 25	98 4	3,635 2	
LHMB	12 3	12 3	12 3	12 3	0 070	12 3	252 4	
MHMB	94 7	94.7	94 7	94 7	0 24	94 7	3,414 6	
HHMB	98 3	98 3	98 3	98 3	0 25	98 3	3,624 2	
LHHB	8.5	8 5	8 5	8 5	0 050	8 5	174 9	
MHHB	95 9	95 9	95 9	95 9	0 24	95 9	3,487 5	
HHHB	98 4	98 4	98 4	98 4	0 25	98 4	3,633 5	

Appendix G

Emission Rate Estimates
Diffused Air Systems

TABLE G-1
EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - DIFFUSED AIR SYSTEM*

Modeling Parameters	CASE NUMBERS																						
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21**	22***	23****
Area (acres)	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03	6.7E-03
Depth (m)	2	4	5	6	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	2	4	6
Retention time (hours)	4	4	4	4	3	4	5	6	4	4	4	4	4	4	4	4	4	4	4	4	6	4	3
Constituent concentration (ppm)	1000	1000	1000	1000	1000	1000	1000	1000	10	1000	2000	4000	1000	1000	1000	1000	1000	1000	1000	1000	10	1000	4000
Submerged air flow (m^3/sec)	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.03	0.04	0.045	0.05	0.04	0.04	0.04	0.04	0.03	0.04	0.05
Air temperature (°C)	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
Wind speed (mph)	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	5	10	70	1	1	1

* Input assumptions:
- Active biomass = 0.0 g/l
- Biomass solids in = 0.0 m^3/sec
- Fraction agitated = 0.0
- Number of impellers = 1
- Oxygen transfer rating = 3 lb O^2/h·hp
- Power (total) = 75 hp
- Oxygen transfer correction factor = 0.83
- Impeller diameter = 61 cm
- Impeller speed = 126 rad/sec

** Reasonable Best Case (minimum) Emissions (assuming typical source area)
*** Typical Emission Conditions (assuming typical source area)
**** Reasonable Worst Case (maximum) Emissions (assuming typical source area)

Note: If actual input values vary significantly from the above scenarios it is recommended that CHEMDAT6 be used to calculate emission estimates directly

TABLE G-2
EMISSION RATE ESTIMATES (10^6 g/yr) - DIFFUSED AIR SYSTEM

Henry's Law Constant Surrogate	(Case 1)	(Case 2)	(Case 3)	(Case 4)	(Case 5)	(Case 6)	(Case 7)	(Case 8)
MHLB	3.8	3.9	3.9	3.9	3.9	3.9	3.9	3.9
HHLB	110.0	205.4	248 5	289.0	262.3	205.4	168 8	143.2
LHMB	0.086	0.086	0.086	0.086	0.086	0.086	0.086	0 086
MHMB	6.2	6.4	6.4	6.4	6.4	6.4	6.3	6.3
HHMB	42.3	51.5	53.8	55.5	54.4	51.5	48 8	46.4
LHHB	0.055	0.055	0.055	0.055	0.055	0.055	0.055	0 055
MHHB	7.8	8.1	8.2	8.2	8.2	8.1	8.0	8 0
HHHB	83.4	128.9	144.6	157.5	149.2	128.9	113.4	101 3

Henry's Law Constant Surrogate	(Case 9)	(Case 10)	(Case 11)	(Case 12)	(Case 13)	(Case 14)	(Case 15)	(Case 16)
MHLB	0.039	3.9	7.8	15.6	3.6	3.9	4.0	4.2
HHLB	2.0	205.4	410.8	821.5	196.8	205.4	208.4	210.9
LHMB	8.6E-04	0.086	0.17	0.34	0.084	0.086	0.087	0.088
MHMB	0.064	6.4	12.8	25.5	5.9	6.4	6 6	6.9
HHMB	0.51	51.5	102.9	205.9	41.6	51.5	56.0	60 3
LHHB	5.5E-04	0.055	0.11	0.22	0.053	0.055	0.056	0 057
MHHB	0.081	8.1	16.2	32.4	7.3	8.1	8.5	8.9
HHHB	1.3	128 9	257 8	515 5	112.3	128 9	135 6	141·6

Henry's Law Constant Surrogate	1 Year (Case 17)	5 Years (Case 18)	10 Years (Case 19)	70 Years (Case 20)	Case 21	Case 22	Case 23	
MHLB	3.9	3.9	3.9	3.9	0.035	3.9	16.8	
HHLB	205.4	205.4	205.4	205.4	0.74	205.4	1522.0	
LHMB	0.086	0.086	0.086	0.086	8.4E-04	0 086	0.35	
MHMB	6.4	6.4	6.4	6.4	0.056	6 4	27.9	
HHMB	51.5	51.5	51.5	51.5	0.31	51 5	276.6	
LHHB	0.055	0.055	0 055	0.055	5.3E-04	0 055	0 23	
MHHB	8.1	8 1	8.1	8.1	0 068	8 1	36 3	
HHHB	128 9	128.9	128 9	128.9	0.58	128 9	808 0	

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Appendix H

Emission Rate Estimates
Land Treatment
(Emissions After Tilling)

TABLE H-1
EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - LAND TREATMENT (EMISSIONS AFTER TILLING)*

Modeling Parameters	CASE NUMBERS																						
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21**	22***	23****
Area (acres)	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2
Annual waste (oil & water) throughput (10^6g/yr)	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800
Oil content of waste(%)	2	10	20	50	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	2	10	50
Constituent of interest content of oil (ppm)	2000	2000	2000	2000	500	2000	5000	10,000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	500	2000	10000
Soil porosity (%)	50	50	50	50	50	50	50	50	43	50	55	65	50	50	50	50	50	50	50	50	43	50	65
Tilling depth (cm)	20	20	20	20	20	20	20	20	20	20	20	20	15	20	40	65	20	20	20	20	65	20	15
Air temperature (°C)	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	5	10	70	1	1	1

* Input assumptions:
- Molecular weight of oil = 282
- Organics (VO) dissolved in water = 0.0
- Biodegradation considered = yes

** Reasonable Best Case (minimum) Emissions (assuming typical source area)
*** Typical Emission Conditions (assuming typical source area)
**** Reasonable Worst Case (maximum) Emissions (assuming typical source area)

Note: If actual input values vary significantly from the above scenarios it is recommended that CHEMDA16 be used to calculate emission estimates directly

TABLE H-2
EMISSION RATE ESTIMATES (10^6 g/yr) - LAND TREATMENT (EMISSION AFTER TILLING)

Raoult's Law Surrogate	(Case 1)	(Case 2)	(Case 3)	(Case 4)	(Case 5)	(Case 6)	(Case 7)	(Case 8)
HVHB	0.071	0.341	0.650	1.431	0.085	0.341	0.853	1.706
HVMB	0.072	0.357	0.708	1.730	0.089	0.357	0.892	1.784
HVLB	0.072	0.359	0.719	1.793	0.090	0.359	0.898	1.796
MVHB	0.044	0.108	0.153	0.243	0.027	0.108	0.271	0.542
MVMB	0.063	0.219	0.338	0.533	0.055	0.219	0.548	1.096
MVLB	0.071	0.338	0.639	1.382	0.085	0.338	0.845	1.690
LVMB	7.92E-04	1.80E-03	2.16E-03	3.60E-03	4.50E-04	1.80E-03	4.50E-03	9.00E-03
VHVHB	0.072	0.356	0.708	1.728	0.089	0.356	0.891	1.782
VHVLB	0.072	0.359	0.719	1.796	0.090	0.359	0.898	1.796
Raoult's Law Surrogate	**(Case 9)**	**(Case 10)**	**(Case 11)**	**(Case 12)**	**(Case 13)**	**(Case 14)**	**(Case 15)**	**(Case 16)**
HVHB	0.334	0.341	0.345	0.349	0.346	0.341	0.325	0.308
HVMB	0.355	0.357	0.357	0.358	0.357	0.357	0.354	0.351
HVLB	0.359	0.359	0.359	0.359	0.359	0.359	0.359	0.359
HVHB	0.091	0.108	0.121	0.147	0.125	0.108	0.077	0.060
MVMB	0.194	0.219	0.235	0.262	0.240	0.219	0.169	0.133
MVLB	0.330	0.338	0.342	0.347	0.343	0.338	0.319	0.300
LVMB	1.44E-03	1.80E-03	1.80E-03	2.52E-03	2.16E-03	1.80E-03	1.08E-03	1.08E-03
VHVHB	0.355	0.356	0.357	0.358	0.357	0.356	0.354	0.350
VHVLB	0.359	0.359	0.359	0.359	0.359	0.359	0.359	0.359
Raoult's Law Surrogate	**(Case 17)**	**(Case 18)**	**(Case 19)**	**(Case 20)**	**(Case 21)**	**(Case 22)**	**(Case 23)**	
HVHB	0.341	0.341	0.341	0.341	0.017	0.341	8.118	
HVMB	0.357	0.357	0.357	0.357	0.018	0.357	8.847	
HVLB	0.359	0.359	0.359	0.359	0.018	0.359	8.982	
MVHB	0.108	0.108	0.108	0.108	0.006	0.108	1.908	
MVMB	0.219	0.219	0.219	0.219	0.011	0.219	4.194	
MVLB	0.338	0.338	0.338	0.338	0.017	0.338	7.974	
LVMB	1.80E-03	1.80E-03	1.80E-03	1.80E-03	9.00E-05	1.80E-03	2.70E-02	
VHVHB	0.356	0.356	0.356	0.356	0.018	0.356	8.838	
VHVLB	0.359	0.359	0.359	0.359	0.018	0.359	8.982	

Appendix I

Emission Rate Estimates
Oil Film Surface on Land Treatment Units

TABLE I-1
EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - OIL FILM SURFACE ON LAND TREATMENT UNITS*

Modeling Parameters	CASE NUMBERS																		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17**	18***	19****
Area (acres)	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2
Depth of oil film (m)	7.2E-04	7.2E-03	7.2E-02	7.2E-01	7.2E-02	7.2E-02	7.2E-02	7.2E-02	7.2E-02	7.2E-02	7.2E-02	7.2E-02	7.2E-02	7.2E-02	7.2E-02	7.2E-02	7.2E-04	7.2E-02	7.2E-01
Number of Applications per year	365	365	365	365	20	50	365	730	365	365	365	365	365	365	365	365	20	365	730
Constituent concentration in oil (ppm)	200	200	200	200	200	200	200	200	100	200	1000	5000	200	200	200	200	100	200	5000
Air temperature (°C)	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
Wind speed (mph)	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1	1	1	5	10	70	1	1	1

* Input assumptions:
- Flow = 0.0 m^3/sec
- Oil (fraction of waste) = 1.0
- Molecular weight of oil = 282
- Density of oil = 1.0 g/cc

** Reasonable Best Case (minimum) Emissions (assuming typical source area)
*** Typical Emission Conditions (assuming typical source area)
**** Reasonable Worst Case (maximum) Emissions (assuming typical source area)

Note: If actual input values vary significantly from the above scenarios it is recommended that CHEMDAT6 be used to calculate emisison estimates directly.

TABLE I-2
EMISSION RATE ESTIMATES (10^6 g/yr) - OIL FILM SURFACE ON LAND TREATMENT UNIT

Raoult's Law Surrogate	(Case 1)	(Case 2)	(Case 3)	(Case 4)	(Case 5)	(Case 6)	(Case 7)	(Case 8)
HVHB	1.3	13.1	131.4	1,205.2	7.2	18.0	131.4	262.8
HVMB	1.3	13.1	131.4	1,225.5	7.2	18.0	131.4	262.8
HVLB	1.3	13.1	131.4	1,242.0	7.2	18.0	131.4	262.8
MVHB	1.3	12.2	30.8	34.7	7.1	15.4	30.8	32.7
MVMB	1.3	11.0	22.0	23.8	6.9	13.2	22.0	22.8
MVLB	1.3	12.3	31.2	35.1	7.1	15.5	31.2	33.1
LVMB	1.55E-03	1.54E-03	1.45E-03	1.31E-03	1.54E-03	1.53E-03	1.45E-03	1.31E-03
VHVHB	1.3	13.1	131.4	1,314.0	7.2	18.0	131.4	262.8
VHVLB	1.3	13.1	131.4	1,314.0	7.2	18.0	131.4	262.8
Raoult's Law Surrogate	**(Case 9)**	**(Case 10)**	**(Case 11)**	**(Case 12)**	**1 Year (Case 13)**	**5 Years (Case 14)**	**10 Years (Case 15)**	**70 Years (Case 16)**
HVHB	65.7	131.4	657.0	3,285.0	131.4	131.4	131.4	131.4
HVMB	65.7	131.4	657.0	3,285.0	131.4	131.4	131.4	131.4
HVLB	65.7	131.4	657.0	3,285.0	131.4	131.4	131.4	131.4
HVHB	15.4	30.8	154.2	771.1	30.8	30.8	30.8	30.8
MVMB	11.0	22.0	109.9	549.7	22.0	22.0	22.0	22.0
MVLB	15.6	31.2	155.9	779.5	31.2	31.2	31.2	31.2
LVMB	7.23E-04	1.45E-03	7.23E-03	0.036	1.45E-03	1.45E-03	1.45E-03	1.45E-03
VHVHB	65.7	131.4	657.0	3,285.0	131.4	131.4	131.4	131.4
VHVLB	65.7	131.4	657.0	3,285.0	131.4	131.4	131.4	131.4
Raoult's Law Surrogate	**(Case 17)**	**(Case 18)**	**(Case 19)**					
HVHB	0.036	131.4	46,072.4					
HVMB	0.036	131.4	47,942.7					
HVLB	0.036	131.4	49,634.6					
MVHB	0.036	30.8	846.7					
MVMB	0.036	22.0	580.7					
MVLB	0.036	31.2	857.3					
LVMB	7.62E-04	1.45E-03	.038					
VHVHB	0.036	131.4	65,699.1					
VHVLB	0.036	131.4	65,699.7					

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Appendix J

Emission Rate Estimates
Closed Landfills

TABLE J-1
EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - CLOSED LANDFILL (VENTED)*

Modeling Parameters	CASE NUMBERS																						
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21**	22***	23****
Area (acres)	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Waste-bed thickness (ft)	15	30	60	120	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	120
Cap thickness (ft)	3.5	3.5	3.5	3.5	2	3.5	5	6	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	6	3.5	2
Weight percent organics (VO) in waste	40	40	40	40	40	40	40	40	10	40	60	90	40	40	40	40	40	40	40	40	10	40	90
Air porosity of fixed waste (%)	25	25	25	25	25	25	25	25	25	25	25	25	5	25	50	75	25	25	25	25	5	25	75
Waste liquid density (g/cm³)	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Cap air porosity (%)	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8
Cap total porosity (%)	41	41	41	41	41	41	41	41	41	41	41	41	41	41	41	41	41	41	41	41	41	41	41
Temperature beneath cap (°C)	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
Typical barometric pressure (mb)	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013	1013
Typical barometric pressure drop (mb)	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Air temperature (°C)	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	5	10	70	1	1	1

* Input assumptions:
- 100% of the organics in waste is the constituent of interest
- Weight percent oil in waste = 0.0% (fraction = 0.0)
- Weight percent water in waste = 100%-organics (fraction = 1.0-organics)
- Barometric pumping time = 86,400 sec
- Molecular weight oil = 147
- CHEMDAT6 CC/GVOC conversion factor = 1750
- Active biomass = 0.0 g/cc
- Organics dissolved in water = 0 (i.e., use Raoult's Law)
- Rho liquid density = 1.0 g/cm3
- Molecular weight of liquid = 18

** Reasonable Best Case (minimum) Emissions (assuming typical source area)
*** Typical Emission Conditions (assuming typical source area)
**** Reasonable Worst Case (maximum) Emissions (assuming typical source area)

Note: If actual input values vary significantly from the above scenarios it is recommended that CHEMDAT6 be used to calculate emission estimates directly

TABLE J-2
EMISSION RATE ESTIMATES (10^6 g/yr) - CLOSED LANDFILL (VENTED)

Raoult's Law Surrogate	(Case 1)	(Case 2)	(Case 3)	(Case 4)	(Case 5)	(Case 6)	(Case 7)	(Case 8)
HVHB	2.44E+01	4.44E+01	8.44E+01	1.64E+02	2.78E+01	2.44E+01	2.31E+01	2.26E+01
HVMB	2.24E+01	3.96E+01	7.40E+01	1.43E+02	2.63E+01	2.24E+01	2.08E+01	2.02E+01
HVLB	4.69E+01	8.60E+01	1.64E+02	3.20E+02	5.29E+01	4.70E+01	4.46E+01	4.37E+01
MVHB	4.45E-01	8.24E-01	1.58E+00	3.10E+00	4.94E-01	4.45E-01	4.25E-01	4.18E-01
MVMB	3.98E-01	7.46E-01	1.44E+00	2.83E+00	4.36E-01	3.98E-01	3.83E-01	3.77E-01
MVLB	8.08E-01	1.51E+00	2.92E+00	5.73E+00	8.88E-01	8.08E-01	7.77E-01	7.64E-01
LVMB	1.55E-05	2.83E-05	5.39E-05	1.05E-04	1.76E-05	1.55E-05	1.47E-05	1.44E-05
VHVHB	1.19E+02	2.15E+02	4.09E+02	7.96E+02	1.35E+02	1.19E+02	1.12E+02	1.10E+02
VHVLB	2.64E+02	4.77E+02	9.03E+02	1.76E+03	3.02E+02	2.64E+02	2.49E+02	2.43E+02
Raoult's Law Surrogate	**(Case 9)**	**(Case 10)**	**(Case 11)**	**(Case 12)**	**(Case 13)**	**(Case 14)**	**(Case 15)**	**(Case 16)**
HVHB	2.44E+01	2.44E+01	2.44E+01	2.44E+01	8.45E+00	2.44E+01	4.44E+01	6.44E+01
HVMB	2.24E+01	2.24E+01	2.24E+01	2.24E+01	8.63E+00	2.24E+01	3.96E+01	5.68E+01
HVLB	4.68E+01	4.70E+01	4.70E+01	4.70E+01	1.57E+01	4.70E+01	8.60E+01	1.25E+02
MVHB	4.45E-01	4.45E-01	4.45E-01	4.45E-01	1.41E-01	4.45E-01	8.25E-01	1.20E+00
MVMB	3.98E-01	3.98E-01	3.98E-01	3.98E-01	1.20E-01	3.98E-01	7.46E-01	1.09E+00
MVLB	8.08E-01	8.08E-01	8.08E-01	8.08E-01	2.46E-01	8.08E-01	1.51E+00	2.21E+00
LVMB	1.55E-05	1.55E-05	1.55E-05	1.55E-05	5.29E-06	1.55E-05	2.83E-05	4.11E-05
VHVHB	1.18E+02	1.19E+02	1.19E+02	1.19E+02	4.14E+01	1.19E+02	2.15E+02	3.11E+02
VHVLB	2.61E+02	2.64E+02	2.64E+02	2.65E+02	9.40E+01	2.64E+02	4.75E+02	6.85E+02
Raoult's Law Surrogate	**1 Year (Case 17)**	**5 Years (Case 18)**	**10 Years (Case 19)**	**70 Years (Case 20)**	**(Case 21)**	**(Case 22)**	**(Case 23)**	
HVHB	2.44E+01	2.44E+01	2.44E+01	2.38E+01	6.59E+00	2.44E+01	4.88E+02	
HVMB	2.24E+01	2.24E+01	2.23E+01	2.18E+01	6.47E+00	2.24E+01	4.22E+02	
HVLB	4.70E+01	4.68E+01	4.66E+01	4.45E+01	1.24E+01	4.70E+01	9.51E+02	
MVHB	4.45E-01	4.45E-01	4.45E-01	4.45E-01	1.14E-01	4.45E-01	9.22E+00	
MVMB	3.98E-01	3.98E-01	3.98E-01	3.98E-01	9.89E-02	3.98E-01	8.44E+00	
MVLB	8.08E-01	8.08E-01	8.08E-01	8.08E-01	2.02E-01	8.08E-01	1.70E+01	
LVMB	1.55E-05	1.55E-05	1.55E-05	1.55E-05	4.15E-06	1.55E-05	3.12E-04	
VHVHB	1.19E+02	1.18E+02	1.17E+02	1.08E+02	3.22E+01	1.19E+02	2.36E+03	
VHVLB	2.64E+02	2.60E+02	2.54E+02	1.98E+02	7.23E+01	2.64E+02	5.20E+03	

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Appendix K

Emission Rate Estimates
Open Landfills

TABLE K-1
EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - OPEN LANDFILL*

Modeling Parameters	CASE NUMBERS																						
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21**	22***	23****
Area (acres)	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Waste-bed thickness (ft)	3	7.5	15	30	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	3	7.5	30
Constituent content of waste (%)	40	40	40	40	10	40	60	90	40	40	40	40	40	40	40	40	40	40	40	40	10	40	90
Air porosity of fixed waste (%)	25	25	25	25	25	25	25	25	5	25	35	50	25	25	25	25	25	25	25	25	5	25	50
Total porosity of fixed waste (%)	50	50	50	50	50	50	50	50	50	50	50	50	10	25	50	75	50	50	50	50	75	50	10
Waste liquid density (g/cm^3)	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Air temperature (°C)	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	5	10	70	1	1	1

* Input assumptions
- Organic (VO) concentration of waste = 1,000,000 ppmw
- Molecular weight of oil = 147
- Organics dissolved in water = 0 (i.e., no)
- Biodegradation = 0 (i.e., no)

** Reasonable Best Case (minimum) Emissions (assuming typical source area)

*** Typical Emission Conditions (assuming typical source area)

**** Reasonable Worst Case (maximum) Emissions (assuming typical source area)

Note: If actual values vary significantly from the above scenarios it is recommended that CHEMDAT6 be used to calculate emission estimates directly

TABLE K-2
EMISSION RATE ESTIMATES (10^6 g/yr) - OPEN LANDFILL

Raoult's Law Surrogate	(Case 1)	(Case 2)	(Case 3)	(Case 4)	(Case 5)	(Case 6)	(Case 7)	(Case 8)
HVHB	769.2	766.2	781.2	781.2	386.9	766.2	946.5	1149.3
HVMB	841.3	841.3	841.3	841.3	420.7	841.3	1036.6	1250.7
HVLB	817.3	811.3	811.3	841.3	409.4	811.3	991.6	1216.9
MVHB	78.1	75.1	90.1	60.1	37.6	75.1	90.1	101.4
MVMB	60.1	60.1	60.1	60.1	30.0	60.1	67.6	101.4
MVLB	78.1	75.1	90.1	60.1	37.6	75.1	90.1	101.4
LVMB	0.5	0.6	0.6	0.6	0.3	0.6	0.7	0.7
VHVHB	2361.7	2358.7	2373.8	2343.7	1179.4	2358.7	2884.6	3549.4
VHVLB	2518.0	2509.0	2524.0	2524.0	1258.2	2509.0	3087.4	3786.0
Raoult's Law Surrogate	**(Case 9)**	**(Case 10)**	**(Case 11)**	**(Case 12)**	**(Case 13)**	**(Case 14)**	**(Case 15)**	**(Case 16)**
HVHB	30.0	766.2	1592.5	3455.5	3846.1	1547.5	766.2	510.8
HVMB	30.0	841.3	1742.8	3786.0	4206.7	1682.7	841.3	555.9
HVLB	30.0	811.3	1697.7	3680.8	4086.5	1637.6	811.3	540.9
MVHB	2.4	75.1	165.3	345.5	375.6	150.2	75.1	45.1
MVMB	2.0	60.1	120.2	270.4	300.5	120.2	60.1	45.1
MVLB	2.3	75.1	150.2	330.5	375.6	150.2	75.1	45.1
LVMB	0.02	0.6	1.1	2.4	2.7	1.1	0.6	0.3
VHVHB	75.1	2358.7	4882.7	10336.4	11297.9	4717.5	2358.7	1577.5
VHVLB	75.1	2509.0	5213.3	10907.3	11853.8	5033.0	2509.0	1682.7
Raoult's Law Surrogate	**1 year (Case 17)**	**5 years (Case 18)**	**10 years (Case 19)**	**70 years (Case 20)**	**(Case 21)**	**(Case 22)**	**(Case 23)**	
HVHB	766.2	1727.7	2433.9	6445.2	7.9	766.2	25961.1	
HVMB	841.3	1878.0	2659.2	7046.2	8.6	841.3	28395.0	
HVLB	811.3	1832.9	2584.1	6850.9	8.4	811.3	27583.7	
MVHB	75.1	165.3	240.4	646.0	0.8	75.1	2569.1	
MVMB	60.1	135.2	195.3	510.8	0.6	60.1	2028.2	
MVLB	75.1	165.3	240.4	631.0	0.8	75.1	2569.1	
LVMB	0.6	1.2	1.7	4.4	0.01	0.6	17.6	
VHVHB	2358.7	5273.4	7451.8	14558.1	24.1	2358.7	78829.9	
VHVLB	2509.0	5618.9	7917.5	14723.3	25.7	2509.0	83697.6	

Appendix L

Emission Rate Estimates
Wastepiles

TABLE L-1
EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - WASTEPILES*

Modeling Parameters	CASE NUMBERS																						
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21**	22***	23****
Area (acres)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Turnover rate (per year)	730	365	140	52	140	140	140	140	140	140	140	140	140	140	140	140	140	140	140	140	52	140	730
Constituent content of waste (%)	40	40	40	40	10	40	60	90	40	40	40	40	40	40	40	40	40	40	40	40	10	40	90
Air porosity of fixed waste (%)	25	25	25	25	25	25	25	25	5	25	35	50	25	25	25	25	25	25	25	25	5	25	50
Total porosity of fixed waste (%)	50	50	50	50	50	50	50	50	50	50	50	50	10	25	50	75	50	50	50	50	75	50	10
Pile height (m)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Waste liquid density (g/cm^3)	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Air temperature (°C)	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	5	10	70	1	1	1

* Input assumptions:
- Organic (VO) concentration of waste = 1,000,000 ppmw
- Molecular weight of oil = 147
- Organics dissolved in water = 0 (i e , no)
- Biodegradation = 0 (i e , no)

** Reasonable Best Case (minimum) Emissions (assuming typical source area)

*** Typical Emission Conditions (assuming typical source area)

**** Reasonable Worst Case (maximum) Emissions (assuming typical source area)

Note: If actual input values vary significantly from the above scenarios it is recommended that CHEMDAT [illegible] calculate emission estimates directly

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TABLE L-2
EMISSION RATE ESTIMATES (10^6 g/yr) - WASTEPILE

Raoult's Law Surrogate	(Case 1)	(Case 2)	(Case 3)	(Case 4)	(Case 5)	(Case 6)	(Case 7)	(Case 8)
HVHB	595.3	421.1	261.4	159.7	130.6	261.4	320.1	391.7
HVMB	651.6	460.9	284.9	174.4	143.1	284.9	350.2	429.1
HVLB	633.7	447.9	277.0	169.5	139.2	277.0	340.3	416.7
MVHB	59.3	41.9	26.0	15.9	13.0	26.0	31.8	38.9
MVMB	47.6	33.6	20.9	12.7	10.4	20.9	25.6	31.3
MVLB	58.3	41.2	25.5	15.6	12.8	25.5	31.3	38.3
LVMB	0.4	0.3	0.2	0.1	0.1	0.2	0.2	0.3
VHVHB	1824.4	1289.4	799.3	487.9	399.7	799.3	981.3	1199.0
VHVLB	1947.9	1378.6	852.1	520.3	426.7	852.1	1044.6	1282.0
Raoult's Law Surrogate	**(Case 9)**	**(Case 10)**	**(Case 11)**	**(Case 12)**	**(Case 13)**	**(Case 14)**	**(Case 15)**	**(Case 16)**
HVHB	8.0	261.4	540.8	1173.9	1305.8	522.3	261.4	174.1
HVMB	8.8	284.9	593.5	1284.7	1429.8	572.4	284.9	190.7
HVLB	8.5	277.0	575.1	1247.8	1387.6	556.6	277.0	185.2
MVHB	0.8	26.0	53.8	116.6	129.8	52.0	26.0	17.3
MVMB	0.6	20.9	43.3	93.6	104.2	41.7	20.9	13.9
MVLB	0.8	25.5	53.0	114.8	127.7	51.2	25.5	17.0
LVMB	0.01	0.2	0.4	0.8	0.9	0.4	0.2	0.1
VHVHB	24.5	799.3	659.3	3,587.6	4,009.7	1,598.6	799.3	532.9
VHVLB	26.1	852.1	767.4	3,825.0	4,273.5	1,706.8	852.1	569.8
Raoult's Law Surrogate	**(Case 17)**	**(Case 18)**	**(Case 19)**	**(Case 20)**	**(Case 21)**	**(Case 22)**	**(Case 23)**	
HVHB	261.4	261.4	261.4	261.4	1.6	261.4	20,061.7	
HVMB	284.9	284.9	284.9	284.9	1.8	284.9	21,944.4	
HVLB	277.0	277.0	277.0	277.0	1.7	277.0	21,327.1	
MVHB	26.0	26.0	26.0	26.0	0.2	26.0	1,993.8	
MVMB	20.9	20.9	20.9	20.9	0.1	20.9	1,601.8	
MVLB	25.5	25.5	25.5	25.5	0.2	25.5	1,959.9	
LVMB	0.2	0.2	0.2	0.2	0.001	0.2	13.7	
VHVHB	799.3	799.3	799.3	799.3	5.0	799.3	61,419.6	
VHVLB	852.1	852.1	852.1	852.1	5.3	852.1	65,431.9	

Appendix M

Emission Rate Estimates
Fixed Roof Tanks

TABLE M-1
EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - FIXED ROOF TANK

Modeling Parameters	CASE NUMBERS																							
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22*	23**	24***
Tank diameter (ft)	10	20	40	60	100	200	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	20	100	200
Tank height (ft)	40	40	40	40	40	40	10	20	30	40	50	40	40	40	40	40	40	40	40	40	40	40	40	50
Turnovers (per yr)	2674	668	167	74	27	7	107	53	36	27	21	4	21	42	127	212	297	27	27	27	27	668	27	59
Throughput (10^6 gal/yr)	63	63	63	63	63	63	63	63	63	63	63	10	50	100	300	500	700	63	63	63	63	63	63	700
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	5	10	70	1	1	1

* Reasonable Best Case (minimum) Emissions (assuming typical tank size)
** Typical Emission Conditions (assuming typical tank size)
*** Reasonable Worst Case (maximum) Emissions (assuming typical tank size)

Note: If acutal input values vary significantly from the above scenarios it is recommended that AP-42 be used to calculate emission estimates directly

TABLE M-2
EMISSION RATE ESTIMATES (10^6 g/yr) - FIXED ROOF TANK

Raoult's Law Surrogate	(Case 1)		(Case 2)		(Case 3)		(Case 4)		(Case 5)		(Case 6)		(Case 7)		(Case 8)	
	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working
HVHB*																
HVMB*																
HVLB*																
MVHB	1.6E-02	9.3E-01	9.8E-02	9.3E-01	3.6E-01	1.4E+00	7.3E-01	2.7E+00	1.8E+00	3.9E+00	5.9E+00	3.9E+00	8.7E-01	1.8E+00	1.2E+00	2.7E+00
MVMB	1.6E-02	8.5E-01	9.8E-02	8.5E-01	3.6E-01	1.2E+00	7.3E-01	2.5E+00	1.8E+00	3.5E+00	5.8E+00	3.5E+00	8.7E-01	1.6E+00	1.2E+00	2.5E+00
MVLB	2.9E-02	1.7E+00	1.8E-01	1.7E+00	6.5E-01	2.5E+00	1.3E+00	5.0E+00	3.2E+00	7.1E+00	1.0E+01	7.1E+00	1.6E+00	3.3E+00	2.2E+00	5.0E+00
LVMB	1.4E-05	3.1E-05	8.5E-05	3.1E-05	3.2E-04	4.5E-05	6.4E-04	9.1E-05	1.5E-03	1.3E-04	5.1E-03	1.3E-04	7.6E-04	6.0E-05	1.1E-03	9.1E-05
VHVHB*																
VHVLB*																

Raoult's Law Surrogate	(Case 9)		(Case 10)		(Case 11)		(Case 12)		(Case 13)		(Case 14)		(Case 15)		(Case 16)	
	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working
HVHB*																
HVMB*																
HVLB*																
MVHB	1.5E+00	3.9E+00	1.8E+00	3.9E+00	2.0E+00	3.9E+00	1.8E+00	6.1E-01	1.8E+00	3.1E+00	1.8E+00	4.9E+00	1.8E+00	8.4E+00	1.8E+00	9.2E+00
MVMB	1.5E+00	3.5E+00	1.8E+00	3.5E+00	2.0E+00	3.5E+00	1.8E+00	5.6E-01	1.8E+00	2.8E+00	1.8E+00	4.5E+00	1.8E+00	7.7E+00	1.8E+00	8.4E+00
MVLB	2.7E+00	7.1E+00	3.2E+00	7.1E+00	3.5E+00	7.1E+00	3.2E+00	1.1E+00	3.2E+00	5.7E+00	3.2E+00	9.1E+00	3.2E+00	5.9E+01	3.2E+00	1.7E+01
LVMB	1.3E-03	1.3E-04	1.5E-03	1.3E-04	1.7E-03	1.3E-04	1.5E-03	2.1E-05	1.5E-03	1.0E-04	1.5E-03	1.7E-04	1.5E-03	2.8E-04	1.5E-03	3.1E-04
VHVHB*																
VHVLB*																

Raoult's Law Surrogate	(Case 17)		(Case 18)		(Case 19)		(Case 20)		(Case 21)		(Case 22)		(Case 23)		(Case 24)	
	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working	Breathing	Working
HVHB*																
HVMB																
HVLB*																
MVHB	1.8E+00	1.3E+01	1.8E+00	3.9E+00	1.8E+00	3.9E+00	1.8E+00	3.9E+00	1.8E+00	3.9E+00	9.8E-02	9.3E-01	1.8E+00	3.9E+00	6.6E+00	3.0E+01
MVMB	1.8E+00	1.2E+01	1.8E+00	3.5E+00	1.8E+00	3.5E+00	1.8E+00	3.5E+00	1.8E+00	3.5E+00	9.8E-02	8.5E-01	1.8E+00	3.5E+00	6.5E+00	2.8E+01
MVLB	3.2E+00	2.4E+01	3.2E+00	7.1E+00	3.2E+00	7.1E+00	3.2E+00	7.1E+00	3.2E+00	7.1E+00	1.8E-01	1.7E+00	3.2E+00	7.1E+00	1.2E+01	5.6E+01
LVMB	1.5E-03	4.3E-04	1.5E-03	1.3E-04	1.5E-03	1.3E-04	1.5E-03	1.3E-04	1.5E-03	1.3E-04	8.5E-05	3.1E-05	1.5E-03	1.3E-04	5.7E-03	1.0E-03
VHVHB*																
VHVLB*																

*This type of tank is not typically used for materials with this high vapor pressure.

Appendix N

Emission Rate Estimates
Floating Roof Tanks

TABLE N-1
EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATION - FLOATING ROOF TANK

Modeling Parameters	CASE NUMBERS																											
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26*	27**	28***
Rim seal class (see Table J-3)	A	B	C	D	E	F	G	H	H	H	H	H	H	H	H	H	H	H	H	H	H	H	H	H	H	H	H	H
Shell condition (see Table J-4)	A	A	A	A	A	A	A	A	A	B	C	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	C
Average liquid density (lb/gal)	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	5.6	7.6	9.6	11.6	13.4	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	6.1	5.6	6.1	13.4
Tank diameter (ft)	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	30	60	100	140	180	100	100	100	100	30	100	180
Tank throughput (10^6 gal/yr)	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63	63
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	15	10	70	1	1	1	1

* Estimated Best Case (minimum) Emissions (assuming typical tank size)
** Typical Emission Conditions (assuming typical tank size)
*** Estimated Worst Case (maximum) Emissions (assuming typical tank size)

Note: If actual input values vary significantly from the above scenarios it is recommended that AP-42 be used to calculate emission estimates directly

TABLE N-2
EMISSION RATE ESTIMATES (10^6 g/yr) - FLOATING ROOF TANK

Raoult's Law Surrogates	Case 1			Case 2			Case 3			Case 4			Case 5			Case 6		
	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting
HVHB*																		
HVMB*																		
HVLB*																		
MVHB	1.3E-02	6.2E-02	3.0E-02	3.5E-02	6.2E-02	3.0E-02	5.5E-02	6.2E-02	3.0E-02	9.6E-02	6.2E-02	3.0E-02	1.8E-01	6.2E-02	3.0E-02	3.3E-01	6.2E-02	3.0E-02
MVMB	1.2E-02	6.2E-02	2.8E-02	3.2E-02	6.2E-02	2.8E-02	5.1E-02	6.2E-02	2.8E-02	8.8E-02	6.2E-02	2.8E-02	1.6E-01	6.2E-02	2.8E-02	3.1E-01	6.2E-02	2.8E-02
MVLB	2.4E-02	6.2E-02	5.6E-02	6.4E-02	6.2E-02	5.6E-02	1.0E-01	6.2E-02	5.6E-02	1.8E-01	6.2E-02	5.6E-02	3.3E-01	6.2E-02	5.6E-02	6.2E-01	6.2E-02	5.6E-02
LVMB	4.4E-07	6.2E-02	1.0E-06	1.2E-06	6.2E-02	1.0E-06	1.9E-06	6.2E-02	1.0E-06	3.2E-06	6.2E-02	1.0E-06	6.0E-06	6.2E-02	1.0E-06	1.1E-05	6.2E-02	1.0E-06
VHVHB*																		
VHVLB*																		

Raoult's Law Surrogates	Case 7			Case 8			Case 9			Case 10			Case 11			Case 12		
	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting
HVHB*																		
HVMB*																		
HVLB*																		
MVHB	6.2E-01	6.2E-02	3.0E-02	1.0E+00	6.2E-02	3.0E-02	1.0E+00	6.2E-02	3.0E-02	1.0E+00	3.1E-01	3.0E-02	1.0E+00	6.2E+00	3.0E-02	1.0E+00	5.7E-02	3.0E-02
MVMB	5.7E-01	6.2E-02	2.8E-02	9.5E-01	6.2E-02	2.8E-02	9.5E-01	6.2E-02	2.8E-02	9.5E-01	3.1E-01	2.8E-02	9.5E-01	6.2E+00	2.8E-02	9.5E-01	5.7E-02	2.8E-02
MVLB	1.1E+00	6.2E-02	5.6E-02	1.9E+00	6.2E-02	5.6E-02	1.9E+00	6.2E-02	5.6E-02	1.9E+00	3.1E-01	5.6E-02	1.9E+00	6.2E+00	5.6E-02	1.9E+00	5.7E-02	5.6E-02
LVMB	2.1E-05	6.2E-02	1.0E-06	3.5E-05	6.2E-02	1.0E-06	3.5E-05	6.2E-02	1.0E-06	3.5E-05	3.1E-01	1.0E-06	3.5E-05	6.2E+00	1.0E-06	3.5E-05	5.7E-02	1.0E-06
VHVHB*																		
VHVLB*																		

* This type of tank is not typically used for materials with this high vapor pressure

TABLE N-2
EMISSION RATE ESTIMATES (10^6 g/yr) - FLOATING ROOF TANK (CONTINUED)

Raoult's Law Surrogates	Case 13			Case 14			Case 15			Case 16			Case 17			Case 18		
	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting
HVHB*																		
HVMB*																		
HVLB*																		
MVHB	1.0E+00	7.8E-02	3.0E-02	1.0E+00	9.8E-02	3.0E-02	1.0E+00	1.2E-01	3.0E-02	1.0E+00	1.4E-01	3.0E-02	3.1E-01	2.3E-01	3.0E-02	6.2E-01	1.1E-01	3.0E-02
MVMB	9.5E-01	7.8E-02	2.8E-02	9.5E-01	9.8E-02	2.8E-02	9.5E-01	1.2E-01	2.8E-02	9.5E-01	1.4E-01	2.8E-02	2.9E-01	2.3E-01	2.8E-02	5.7E-01	1.1E-01	2.8E-02
MVLB	1.9E+00	7.8E-02	5.6E-02	1.9E+00	9.8E-02	5.6E-02	1.9E+00	1.2E-01	5.6E-02	1.9E+00	1.4E-01	5.6E-02	5.8E-01	2.3E-01	5.6E-02	1.2E+00	1.1E-01	5.6E-02
LVMB	3.5E-05	7.8E-02	1.0E-06	3.5E-05	9.8E-02	1.0E-06	3.5E-05	1.2E-01	1.0E-06	3.5E-05	1.4E-01	1.0E-06	1.1E-05	2.3E-01	1.0E-06	2.1E-05	1.1E-01	1.0E-06
VHVHB*																		
VHVLB*																		

Raoult's Law Surrogates	Case 19			Case 20			Case 21			Case 22			Case 23			Case 24		
	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting
HVHB*																		
HVMB*																		
HVLB*																		
MVHB	1.0E+00	6.2E-02	3.0E-02	1.5E+00	4.4E-02	3.0E-02	1.9E+00	3.4E-02	3.0E-02	1.0E+00	6.2E-02	3.0E-02	1.0E+00	6.2E-02	3.0E-02	1.0E+00	6.2E-02	3.0E-02
MVMB	9.5E-01	6.2E-02	2.8E-02	1.3E+00	4.4E-02	2.8E-02	1.7E+00	3.4E-02	2.8E-02	9.5E-01	6.2E-02	2.8E-02	9.5E-01	6.2E-02	2.8E-02	9.5E-01	6.2E-02	2.8E-02
MVLB	1.9E+00	6.2E-02	5.6E-02	2.7E+00	4.4E-02	5.6E-02	3.5E+00	3.4E-02	5.6E-02	1.9E+00	6.2E-02	5.6E-02	1.9E+00	6.2E-02	5.6E-02	1.9E+00	6.2E-02	5.6E-02
LVMB	3.5E-05	6.2E-02	1.0E-06	4.9E-05	4.4E-02	1.0E-06	6.3E-05	3.4E-02	1.0E-06	3.5E-05	6.2E-02	1.0E-06	3.5E-05	6.2E-02	1.0E-06	3.5E-05	6.2E-02	1.0E-06
VHVHB*																		
VHVLB*																		

* This type of tank is not typically used for materials with this high vapor pressure

TABLE N-2
EMISSION RATE ESTIMATES 10^6 g/yr) - FLOATING ROOF TANK (CONTINUED)

Raoult's Law Surrogates	Case 25			Case 26			Case 27			Case 28		
	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting	Rim	Withdrawal	Fitting
HVHB*												
HVMB*												
HVLB*												
MVHB	1.0E+00	6.2E-02	3.0E-02	3.1E-01	2.2E-01	3.0E-02	1.0E+00	6.2E-02	3.0E-02	1.9E+00	7.4E+00	3.0E-02
MVMB	9.5E-01	6.2E-02	2.8E-02	2.9E-01	2.2E-01	2.8E-02	9.5E-01	6.2E-02	2.8E-02	1.7E+00	7.4E+00	2.8E-02
MVLB	1.9E+00	6.2E-02	5.6E-02	5.8E-01	2.2E-01	5.6E-02	1.9E+00	6.2E-02	5.6E-02	3.5E+00	7.4E+00	5.6E-02
LVMB	3.5E-05	6.2E-02	1.0E-06	1.0E-05	2.2E-01	1.0E-06	3.5E-05	6.2E-02	1.0E-06	6.3E-05	7.4E+00	1.0E-06
VHVHB*												
VHVLB*												

* This type of tank is not typically used for materials with this high vapor pressure.

TABLE N-3
TANK RIM SEAL CLASSES

DESCRIPTION	CLASS
External Floating Roof Tank:	
Metallic shoe seal	
- primary seal only	E (E)*
- with shoe mounted secondary seal	C (D)*
- with rim mounted secondary seal	A (B)*
Liquid mounted resilient seal	
- primary seal only	C
- with weather shield	B
- with rim mounted secondary seal	A
Vapor mounted resilient seal	
- primary seal only	H
- with weather shield	G
with rim mounted secondary seal	F
Internal Floating Roof Tank:	
Liquid mounted resilient seal	
- primary seal only	A
- with rim mounted secondary seal	A
Vapor mounted resilient seal	
- primary seal only	B
- with rim mounted secondary seal	A

*For riveted tank

TABLE N-4
TANK SHELL CONDITIONS

CLASS	DESCRIPTION
A	Light rust
B	Dense rust
C	Gunite lined

Appendix O

Emission Rate Estimates
Variable Vapor Space Tanks

TABLE O-1
EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - VARIABLE VAPOR SPACE TANK

Modeling Parameters	CASE NUMBERS														
	1	2	3	4	5	6	7	8	9	10	11	12	13*	14**	15***
Throughput (10^6 gal/yr)	.5	10	24	42	10	10	10	10	10	10	10	10	10	10	40
Transfers into tank(#/ yr)	60	60	60	60	3	60	120	250	60	60	60	60	60	60	250
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	5	10	70	1	1	1

* Reasonable Best Case (minimum) Emissions (assuming typical tank size)
** Typical Emission Conditions (assuming typical tank size)
*** Reasonable Worst Case (maximum) Emissions (assuming typical tank size)

Note: If actual input values vary significantly from the above scenarios it is recommended that AP-42 be used to calculate emission estimates directly.

TABLE O-2
EMISSION RATE ESTIMATES (10^6 g/yr)-VARIABLE VAPOR SPACE TANK

Raoult's Law Surrogates	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6	Case 7	Case 8
HVHB	7.8E-01	3.0E+01	7.7E+01	1.3E+02	3.1E+01	3.0E+01	2.9E+01	2.8E+01
HVMB	6.7E-01	2.6E+01	6.6E+01	1.2E+02	2.7E+01	2.6E+01	2.5E+01	2.4E+01
HVLB	1.5E+00	5.9E+01	1.5E+02	2.6E+02	6.0E+01	5.9E+01	5.8E+01	5.4E+01
MVHB	1.5E-02	5.7E-01	1.5E+00	2.6E+00	5.9E-01	5.7E-01	5.6E-01	5.3E-01
MVMB	1.4E-02	5.3E-01	1.3E+00	2.3E+00	5.4E-01	5.3E-01	5.1E-01	4.8E-01
MVLB	2.7E-02	1.1E+00	2.7E+00	4.7E+00	1.1E+00	1.1E+00	1.0E+00	9.8E-01
LVMB	5.0E-07	1.9E-05	4.9E-05	8.6E-05	2.0E-05	1.9E-05	1.9E-05	1.8E-05
VHVHB	3.8E+00	1.5E+02	3.7E+02	6.5E+02	1.5E+02	1.5E+02	1.4E+02	1.3E+02
VHVLB	8.3E+00	3.2E+02	8.2E+02	1.4E+03	3.3E+02	3.2E+02	3.1E+02	3.0E+02

Raoult's Law Surrogates	Case 9	Case 10	Case 11	Case 12	Case 13	Case 14	Case 15	
HVHB	3.0E+01	3.0E+01	3.0E+01	3.0E+01	3.0E+01	3.0E+01	1.3E+02	
HVMB	2.6E+01	2.6E+01	2.6E+01	2.6E+01	2.6E+01	2.6E+01	1.1E+02	
HVLB	5.9E+01	5.9E+01	5.9E+01	5.9E+01	5.9E+01	5.9E+01	2.5E+02	
MVHB	5.7E-01	5.7E-01	5.7E-01	5.7E-01	5.7E-01	5.7E-01	2.4E+00	
MVMB	5.3E-01	5.3E-01	5.3E-01	5.3E-01	5.3E-01	5.3E-01	2.2E+00	
MVLB	1.1E+00	1.1E+00	1.1E+00	1.1E+00	1.1E+00	1.1E+00	4.4E+00	
LVMB	1.9E-05	1.9E-05	1.9E-05	1.9E-05	1.9E-05	1.9E-05	8.1E-05	
VHVHB	1.5E+02	1.5E+02	1.5E+02	1.5E+02	1.5E+02	1.5E+02	6.1E+02	
VHVLB	3.2E+02	3.2E+02	3.2E+02	3.2E+02	3.2E+02	3.2E+02	1.3E+03	

Appendix P

Emission Rate Estimates
Particles from Storage Piles

TABLE P-1
EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - PARTICLES FROM STORAGE PILES

Modeling Parameters	CASE NUMBERS																												
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27*	28**	29***
Area of surface of pile (acres)	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Silt content (%)	2	5	10	20	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	5	15	20
% of time windspeed exceeds 12 mph	10	10	10	10	5	10	15	25	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	5	10	25
Days of precipitation ≥ 01 inch per year (see Figure P-1)	60	60	60	60	60	60	60	60	20	60	100	120	60	60	60	60	60	60	60	60	60	60	60	60	60	60	100	60	20
Mean windspeed (mph)	10	10	10	10	10	10	10	10	10	10	10	10	6	10	14	10	10	10	10	10	10	10	10	10	10	10	6	10	14
Moisture content (%)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	.1	3	6	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1	0.5	0.5
Vehicle weight (tons) (assume front end loader)	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	2	4	10	4	4	4	4	4	4	4
Number of wheels on loader	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Throughput (10^2 tons/yr)	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500
Mass fraction of contaminant (ppm)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	5	10	70	1	1	1

* Reasonable Best Case (minimum) Emissions (assuming typical surface area)
** Typical Emission Condition (assuming typical surface area)
*** Reasonable Worst Case (maximum) Emissions (assuming typical surface area)

Note: If actual unit specific parameters are significantly different from the cases provided above it is recommended that emission rates be calculated directly based on the methodology presented in AP-42 (4th Edition - Volume I - Supplement B, September 1988)

Table P-2. Emission Rate Estimates (10^6 g/yr) - Particles from Storage Piles* 1048

Case	Wind Erosion**	Batch Dump***	Vehicle Activity****
1	8.1E-07	1.1E-06	1.4E-07
2	2.0E-06	2.8E-06	3.6E-07
3	4.0E-06	5.6E-06	7.1E-07
4	8.1E-06	1.1E-05	1.4E-06
5	3.1E-06	8.7E-06	1.1E-06
6	6.2E-06	8.7E-06	1.1E-06
7	9.0E-06	8.7E-06	1.1E-06
8	1.5E-05	8.7E-06	1.1E-06
9	6.9E-06	8.7E-06	1.2E-06
10	6.2E-06	8.7E-06	1.1E-06
11	5.2E-06	8.7E-06	9.3E-07
12	5.0E-06	8.7E-06	8.6E-07
13	6.2E-06	5.1E-06	1.1E-06
14	6.2E-06	8.7E-06	1.1E-06
15	6.2E-06	1.2E-05	1.1E-06
16	6.2E-06	8.7E-06	1.1E-06
17	6.2E-06	2.1E-06	1.1E-06
18	6.2E-06	2.3E-07	1.1E-06
19	6.2E-06	5.9E-08	1.1E-06
20	6.2E-06	8.7E-06	6.5E-07
21	6.2E-06	8.7E-06	1.1E-06
22	6.2E-06	8.7E-06	2.1E-06
23	6.2E-06	8.7E-06	1.1E-06
24	6.2E-06	8.7E-06	1.1E-06
25	6.2E-06	8.7E-06	1.1E-06
26	6.2E-06	8.7E-06	1.1E-06
27	8.8E-07	4.2E-07	3.1E-07
28	6.2E-06	8.7E-06	1.1E-06
29	2.3E-05	1.6E-05	1.7E-06

*Particle size of 10 microns assumed (emission rate particle multiplier of 0.5 used, based on pg. 4-7 of Control of Open Fugitive Dust Sources, U.S. EPA, September 1988). Constituent concentration of 1ppm assumed.

**Emission rate estimates for wind erosion based on Equation 3, p. 11.2.3-5 of Compilation of Air Pollutant Emission Factors, Vol.I, (U.S. EPA, September 1985).

***Emission rate estimates for batch dump operations were calculated using Equation 1, p. 11.2.3-3 of Compilation of Air Pollutant Emission Factors, Vol. I. (U.S. EPA, September 1985). Drop height of 21.9 feet and dumping device capacity of 6.375 yd^3 assumed.

****Emission rate estimates for vehicle activity were calculated using Equation 1, p. 11.2.1-1 of Compilation of Air Pollutant Emission Factors, Vol. I, (U.S. EPA, September, 1985) assuming one vehicle in continuous operation for 2,080 hours per year at speed of 3 mph (this low speed assumed to account for loading/unloading in immediate vicinity of the waste pile.) Minor adjustments in emission rates should be implemented if unit-specific vehicle speeds and/or total vehicle miles traveled per year are higher than these assumptions.

MEAN NUMBER OF DAYS WITH 0.01 INCH OR MORE OF PRECIPITATION, ANNUAL

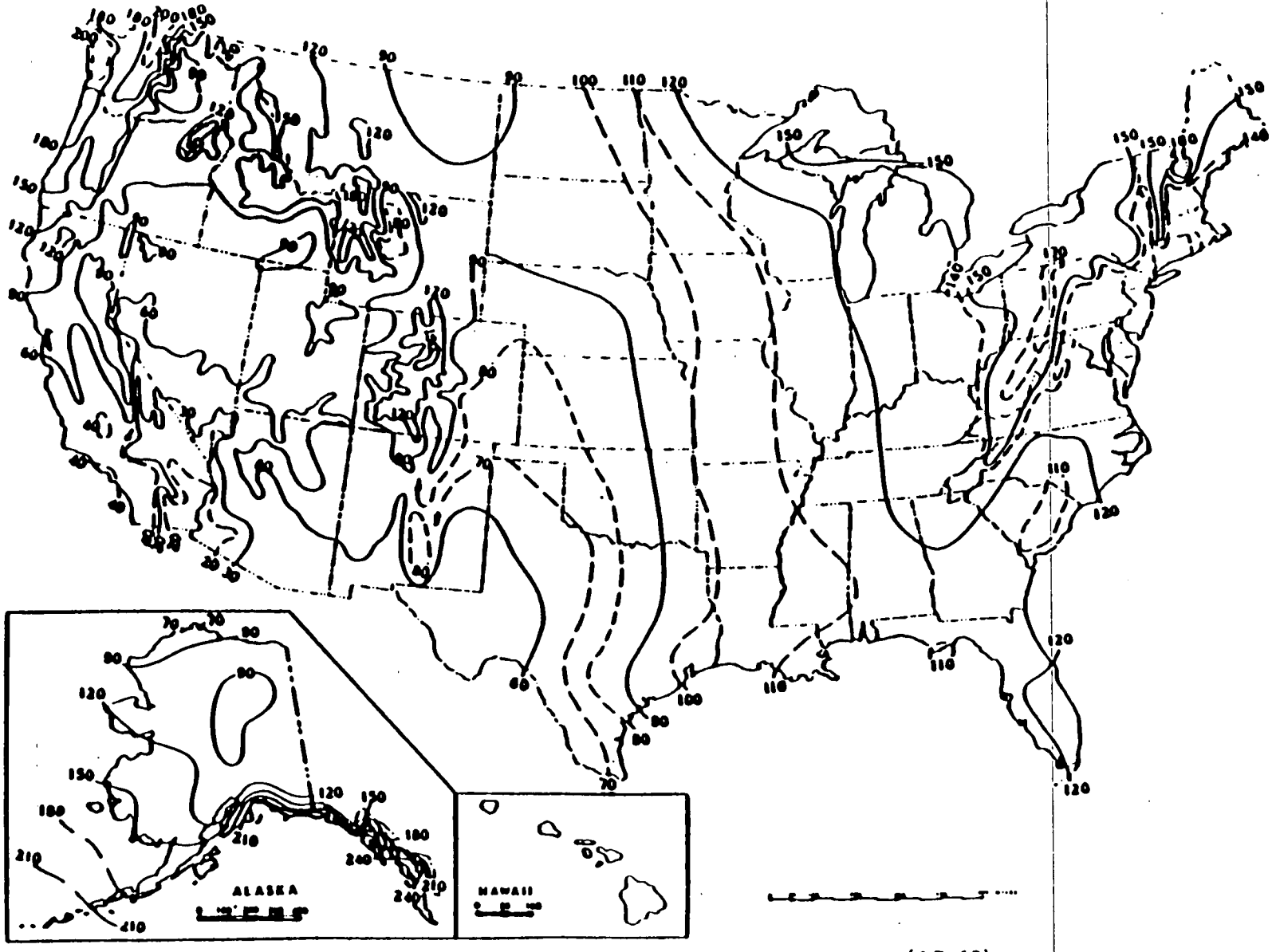

Figure P-1. Map of Precipitation Frequency (AP-42)

Appendix Q

Emission Rate Estimates
Particles from Exposed, Flat, Contaminated Areas

TABLE Q-1
EMISSION RATE MODELING SOURCE SCENARIO CASE SPECIFICATIONS - PARTICLES FROM EXPOSED, FLAT, CONTAMINATED AREAS

Modeling Parameters	CASE NUMBERS																								
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23*	24**	25***
Area of exposed area (acres)	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Silt content (%)	2	5	10	20	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	5	15	20
Surface erodibility (tons/acre-year)(see Table Q-3)	47	47	47	47	38	56	86	134	220	47	47	47	47	47	47	47	47	47	47	47	47	47	38	47	220
Precipitation-evaporation (PE) Index (see Figure Q-1)	100	100	100	100	100	100	100	100	100	20	60	100	200	300	100	100	100	100	100	100	100	100	120	100	20
% of time wind speed exceeds 12 mph	10	10	10	10	10	10	10	10	10	10	10	10	10	10	5	10	15	25	10	10	10	10	5	10	25
Mass fraction of contaminant (ppm)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Calculational period (yrs)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	5	10	70	1	1	1

* Reasonable Best Case (minimum) Emissions (assuming typical surface area)
** Typical Emission Conditions (assuming typical surface area)
*** Reasonable Worst Case (maximum) Emissions (assuming typical surface area)

Note: If actual unit-specific parameters are significantly different from those provided above it is recommended that emission rates be calculated directly using the methodology provided in Control of Open Fugitive Dust Sources (U.S. EPA, September 1988).

TABLE Q-2
EMISSION RATE ESTIMATES (10^6 g/yr) PARTICLES FROM EXPOSED AREAS*

Case	Estimated Emission Rates** (10^6 g/yr)
1	4.8E-08
2	1.2E-07
3	2.4E-07
4	4.8E-07
5	2.9E-07
6	4.3E-07
7	6.7E-05
8	1.0E-06
9	1.7E-06
10	9.1E-06
11	1.0E-06
12	3.6E-07
13	9.1E-06
14	4.0E-08
15	1.8E-07
16	3.6E-07
17	5.5E-07
18	9.1E-07
19	3.6E-07
20	3.6E-07
21	3.6E-07
22	3.6E-07
23	3.4E-08
24	3.6E-07
25	1.4E-04

* Particle size of 10 microns assumed (emission rate particle multiplier of 0.5 used, based on p. 6-9 of Control of Open Fugitive Dust Sources, U.S. EPA, September 1988). Constituent concentration of 1 ppm assumed.

** Emission rate estimates for particles from exposed areas were calculated using Equation 8, p. 4-2 of Fugitive Emissions from Integrated Iron and Steel Plants (U.S. EPA, March 1978).

TABLE Q-3
SOIL ERODIBILITY FOR VARIOUS SOIL TEXTURAL CLASSES*

Predominant Soil Textural Class	Erodibility, tons/acre/year
Sand	220
Loamy sand	134
Sandy loam	86
Clay	86
Silty clay	86
Loam	56
Sandy clay loam	56
Sandy clay	56
Silt loam	47
Clay loam	47
Silty clay loam	38
Silt	38

* U.S. Department of Agriculture, July 1964. Guide for Wind Erosion Control on Cropland in the Great Plains States, Soil Conservation Service.

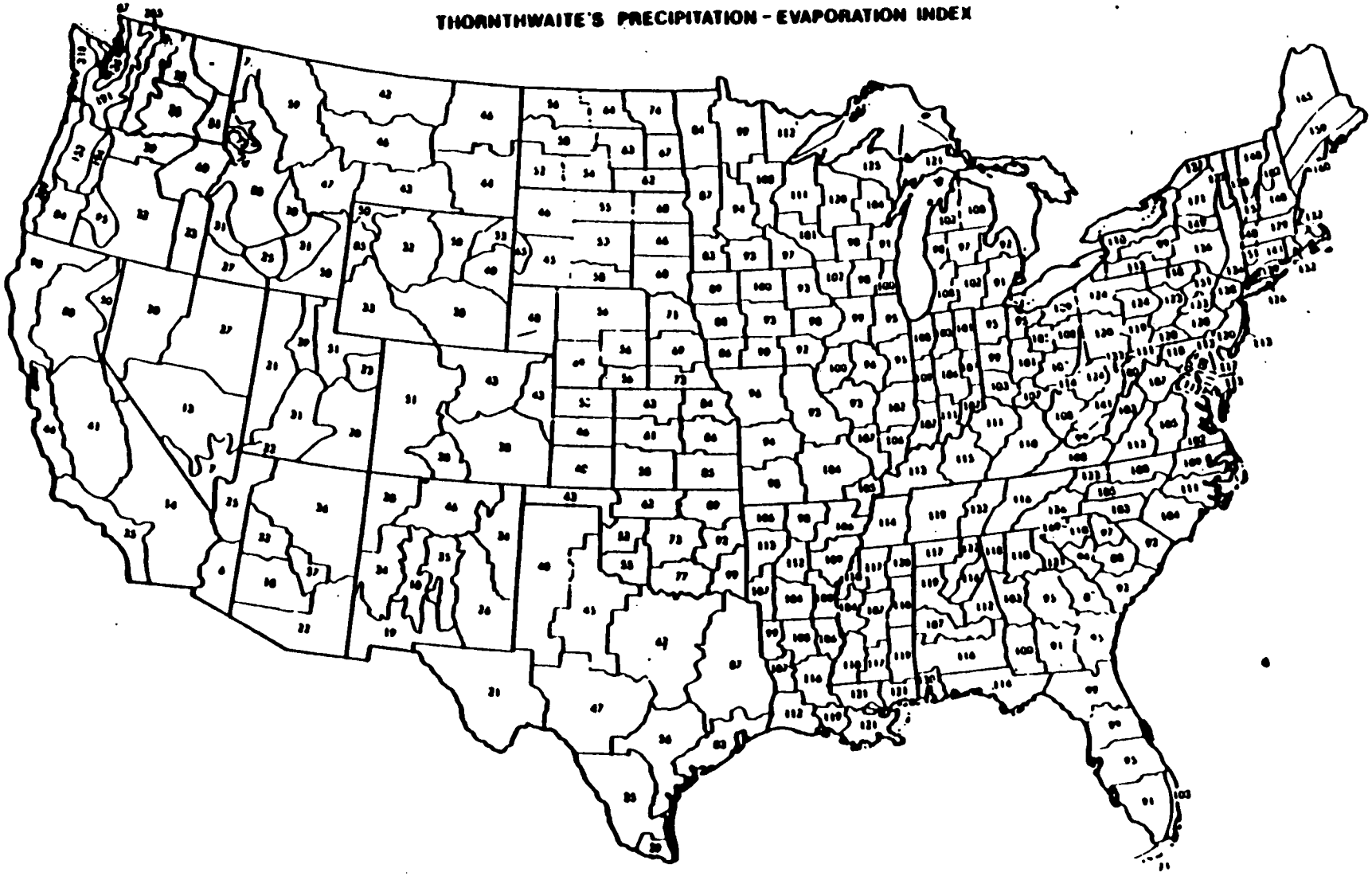

Figure Q-1. Map of PE Index for State Climatic Divisions

U.S. EPA, March 1977. Tec[illegible]al Guidance for Control of Industrial Process Fu[illegible]ve[illegible]rulate Emissions, OAQPS, Research Triangle Pa[illegible]N[illegible]1)

Appendix R

Dispersion Estimates

TABLE R-1
CONCENTRATION ESTIMATION WORKSHEET

Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12	Col 13
Downwind Sector	Instruction A: Input Distance to Receptors** (miles)	Instruction B: Determine Dispersion Factor (Figure R-1)	Instruction C: Assume Annual Downwind Frequency of 100% (percent)	Instruction D: Compute Long-Term Concentration Estimates (μg/m³) Based on Equation 1* (select and circle appropriate surrogate subset, Henry's Law Constant or Raoult's Law or particle case)								
				MHLB or HVHB or particle case	HHLB or HVMB	LHMB or HVLB	MHMB or MVHB	HHMB or MVMB	LHHB or MVLB	MHHB or LVMB	HHHB or VHVHB	---- or VHVLB = Henry's Law Constant Surrogate; = Raoult's Law Surrogate
N												
NNE												
NE												
ENE												
E												
ESE												
SE												
SSE												
S												
SSW												
SW												
WSW												
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WNW												
NW												
NNW												

Health Criteria (μg/m³) Based on RFI Guidance — Toxic Criteria; Carcinogenic Criteria

* Equation 1 Long-Term Concentration Est (μg/m³) = Col 3 x Col 4 x (unit/surrogate-specific Emission Rates, Mg/yr, based on Appendix S Worksheets) x (Conversion Factor = 3.17 x 10^{-5}) x (Safety Factor = 10)
Mg/yr = 10^6g/yr

** Distance from downward unit boundary

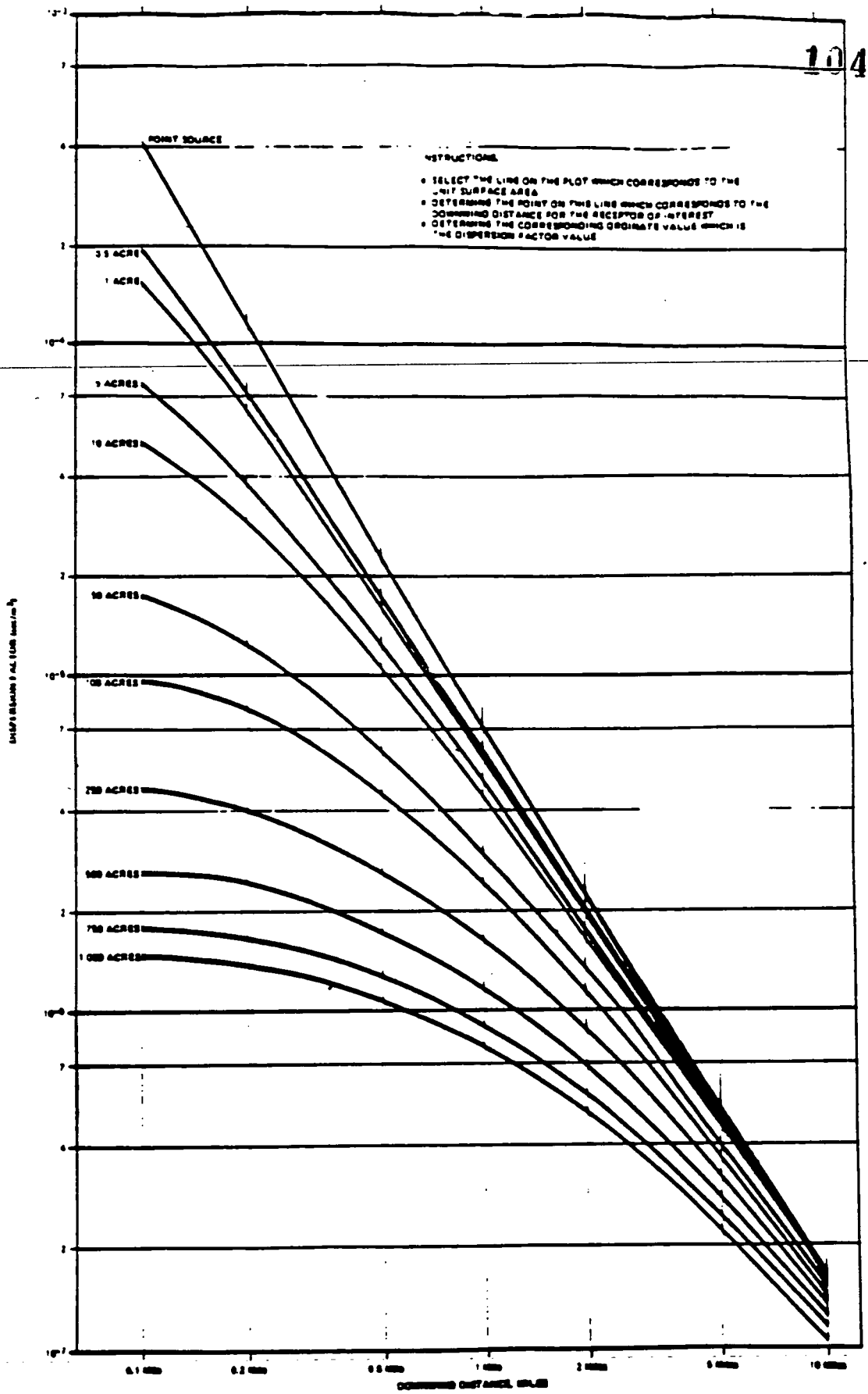

Figure R-1. Atmospheric Dispersion Factors for Typical U.S. Meteorological Conditions (Neutral Stability and 10-MPH Wind Speed)

Appendix S

Emission Rate Estimation Worksheets

TABLE S-1
EMISSION RATE ESTIMATION WORKSHEET - DISPOSAL IMPOUNDMENT

Line	Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11
	Modeling Parameters	Instruction A: Input Unit-Specific Values	Instruction B: Select a Representative Case from Appendix C - Table C-1 (underline selected case)	Instruction C: Determine Surrogate-Specific Scaling Factors**							
				MHLB	HHLB	LHMB	MHMB	HHMB	LHHB	MHHB	HHHB
1	Area*	___ acres	--	--	--	--	--	--	--	--	--
2	Depth*	___ m	1,2,3 or 4	___	___	___	___	___	___	___	___
3	Turnovers*	___ /year	5, 6, 7 or 8	___	___	___	___	___	___	___	___
4	Constituent Concentration*	___ ppm	--	--	--	--	--	--	--	--	--
	INSTRUCTION D: Complete Lines 5-6 and 8			SURROGATE-SPECIFIC VALUES							
5	Account for Area [unit-specific area/(Case 18 area = 2.2 acres)]			___	___	___	___	___	___	___	___
6	Account for Concentration [unit-specific conc./(Case 18 conc. = 1,000 ppm)]			___	___	___	___	___	___	___	___
7	Typical Surrogate-Specific Emission Rate (Case 18), 10^6 g/yr			32.4	32.4	14.1	32.4	32.4	9.4	32.4	32.4
8	Calculate Unit-Specific Emission Rate, 10^6 g/yr (multiply lines #2 x #3 x #5 x #6 x #7)			___	___	___	___	___	___	___	___

* Critical input values
** Scaling Factor determined for Lines 2 and 3 from Appendix C - Emission Rate Estimate from Table C-2 divided by Typical Emission Rate defined in Case 18 (see line 7).

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TABLE S-2
EMISSION RATE ESTIMATION WORKSHEET - STORAGE IMPOUNDMENT

Line	Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11
	Modeling Parameters	Instruction A: Input Unit-Specific Values	Instruction B: Select a Representative Case from Appendix D - Table D-1 (underline selected case)	Instruction C: Determine Surrogate-Specific Scaling Factors**							
				MHLB	HHLB	LHMB	MHMB	HHMB	LHHB	MHHB	HHHB
1	Area*	___ acres	--	--	--	--	--	--	--	--	--
2	Depth*	___ m	1,2,3 or 4	___	___	___	___	___	___	___	___
3	Retention time*	___ days	5, 6, 7 or 8	___	___	___	___	___	___	___	___
4	Constituent Concentration*	___ ppm	--	--	--	--	--	--	--	--	--
	INSTRUCTION D: Complete Lines 5-6 and 8			SURROGATE-SPECIFIC VALUES							
5	Account for Area [unit-specific area/(Case 18 area = 0.4 acres)]			___	___	___	___	___	___	___	___
6	Account for Unit-Specific Concentration [unit-specific conc./(Case 18 conc. = 1,000 ppm)]			___	___	___	___	___	___	___	___
7	Typical Surrogate-Specific Emission Rate (Case 18), 10^6 g/yr			34.0	39.24	3.25	38.10	38.40	1.97	38.74	39.24
8	Calculate Unit-Specific Emission Rate, 10^6 g/yr (multiply lines #2 x #3 x #5 x #6 x #7)			___	___	___	___	___	___	___	___

* Critical input values

** Scaling Factor determined for Lines 2 and 3 from Appendix D - Emission Rate Estimate from Table D-2 divided by Typical Emission Rate defined in Case 18 (see line 7).

TABLE S-3
EMISSION RATE ESTIMATION WORKSHEET - OIL FILM ON STORAGE IMPOUNDMENT

Line	Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12
	Modeling Parameters	Instruction A: Input Unit-Specific Values	Instruction B: Select a Representative Case from Appendix E - Table E-1 (underline selected case)	Instruction C: Determine Surrogate-Specific Scaling Factors**								
				HVHB	HVMB	HVLB	MVHB	MVMB	MVLB	LVMB	VHVHB	VHVLB
1	Area*	____ acres	--	--	--	--	--	--	--	--	--	--
2	Depth of Oil Film*	____ m	1,2,3 or 4	____	____	____	____	____	____	____	____	____
3	Retention Time*	____ days	5, 6, 7 or 8	____	____	____	____	____	____	____	____	____
4	Constituent Concentration*	____ ppm	--	--	--	--	--	--	--	--	--	--
	INSTRUCTION D: Complete Lines 5-6 and 8			SURROGATE-SPECIFIC VALUES								
5	Account for Area [unit-specific area/(Case 18 area = 0.4 acres)]			____	____	____	____	____	____	____	____	____
6	Account for Concentration [unit-specific conc./(Case 18 conc. = 200 ppm)]			____	____	____	____	____	____	____	____	____
7	Typical Surrogate-Specific Emission Rate (Case 18), 10^6 g/yr			0.394	0.394	0.394	0.394	0.389	0.394	1.10E-04	0.394	0.394
8	Calculate Unit-Specific Emission Rate, 10^6 g/yr (multiply lines #2 x #3 x #5 x #6 x #7)			____	____	____	____	____	____	____	____	____

* Critical input values
** Scaling Factor determined for Lines 2 and 3 from Appendix E - Emission Rate Estimate from Table E-2 divided by Typical Emission Rate defined in Case 18 (see line 7).

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TABLE S-4
EMISSION RATE ESTIMATION WORKSHEET - MECHANICALLY AERATED IMPOUNDMENT

Line	Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11
	Modeling Parameters	Instruction A: Input Unit-Specific Values	Instruction B: Select a Representative Case from Appendix F - Table F-1 (underline selected case)	Instruction C: Determine Surrogate-Specific Scaling Factors**							
				MHLB	HHLB	LHMB	MHMB	HHMB	LHHB	MHHB	HHHB
1	Area*	___ acres	--	--	--	--	--	--	--	--	--
2	Depth*	___ m	1,2,3 or 4	___	___	___	___	___	___	___	___
3	Retention Time*	___ days	5, 6, 7 or 8	___	___	___	___	___	___	___	___
4	Constituent Concentration*	___ ppm	--	--	--	--	--	--	--	--	--
5	Fraction Agitated	___	13,14,15 or 16	___	___	___	___	___	___	___	___
	INSTRUCTION D: Complete Lines 6-7 and 9			SURROGATE-SPECIFIC VALUES							
6	Account for Area [unit-specific area/(Case 22 area = 0.4 acres)]			___	___	___	___	___	___	___	___
7	Account for Concentration [unit-specific conc./(Case 22 conc. = 1,000 ppm)]			___	___	___	___	___	___	___	___
8	Typical Surrogate-Specific Emission Rate (Case 22), 10^6 g/yr			90.6	98.4	12.3	94.7	98.3	8.5	95.9	98.4
9	Calculate Unit-Specific Emission Rate, 10^6 g/yr (multiply lines #2 x #3 x #5 x #6 x #7 x #8)			___	___	___	___	___	___	___	___

* Critical input values

** Scaling Factor determined for Lines 2-3 and 5 from Appendix F - Emission Rate Estimate from Table F-2 divided by Typical Emission Rate defined in Case 22 (see line 8).

TABLE S-5
EMISSION RATE ESTIMATION WORKSHEET -

Line	Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11
	Modeling Parameters	Instruction A: Input Unit-Specific Values	Instruction B: Select a Representative Case from Appendix G - Table G-1 (underline selected case)	Instruction C: Determine Surrogate-Specific Scaling Factors**							
				MHLB	HHLB	LHMB	MHMB	HHMB	LHHB	MHHB	HHHB
1	Area*	___ acres	--	--	--	--	--	--	--	--	--
2	Depth*	___ m	1,2,3 or 4	___	___	___	___	___	___	___	___
3	Retention Time*	___ hours	5, 6, 7 or 8	___	___	___	___	___	___	___	___
4	Constituent Concentration*	___ ppm	--	--	--	--	--	--	--	--	--
5	Submerged Air Flow	___ m^3/sec	13,14,15 or 16	___	___	___	___	___	___	___	___
	INSTRUCTION D: Complete Lines 6-7 and 9			SURROGATE-SPECIFIC VALUES							
6	Account for Area [unit-specific area/(Case 22 area = 6.7×10^{-3} acres)]			___	___	___	___	___	___	___	___
7	Account for Concentration [unit-specific conc./(Case 22 conc. = 1,000 ppm)]			___	___	___	___	___	___	___	___
8	Typical Surrogate-Specific Emission Rate (Case 22), 10^6 g/yr			3.9	205.4	0.086	6.4	51.5	0.055	8.1	128.9
9	Calculate Unit-Specific Emission Rate, 10^6 g/yr (multiply lines #2 x #3 x #5 x #6 x #7 x #8)			___	___	___	___	___	___	___	___

* Critical input values
** Scaling Factor determined for Lines 2-3 and 5 from Appendix G - Emission Rate Estimate from Table G-2 divided by Typical Emission Rate defined in Case 22 (see line 8).

TABLE S-6
EMISSION RATE ESTIMATION WORKSHEET - LAND TREATMENT EMISSIONS (AFTER TILLING)

Line	Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12
	Modeling Parameters	Instruction A: Input Unit-Specific Values	Instruction B: Select a Representative Case from Appendix H - Table H-1 (underline selected case)	Instruction C: Determine Surrogate-Specific Scaling Factors**								
				HVHB	HVMB	HVLB	MVHB	MVMB	MVLB	LVMB	VHVHB	VHVLB
1	Annual waste throughput* (water & oil)	___ 10^6 g/yr	--	--	--	--	--	--	--	--	--	--
2	Oil content of waste(%)*	___ percent	1,2,3 or 4	___	___	___	___	___	___	___	___	___
3	Constituent concentration*	___ ppm	5, 6, 7 or 8	___	___	___	___	___	___	___	___	___
4	Soil porosity	___ percent	9, 10, 11 or 12	___	___	___	___	___	___	___	___	___
5	Tilling depth	___ cm	13, 14, 15 or 16	___	___	___	___	___	___	___	___	___
	INSTRUCTION D: Complete Lines 6 and 8			SURROGATE-SPECIFIC VALUES								
6	Account for Unit-Specific Annual Waste Throughput [unit annual waste throughput/(Case 22 = 1,800 10^6 g/yr)]			___	___	___	___	___	___	___	___	___
7	Typical Surrogate-Specific Emission Rate (Case 22), 10^6 g/yr			0.341	0.357	0.359	0.108	0.219	0.338	0.0018	0.356	0.359
8	Calculate Unit-Specific Emission Rate, 10^6 g/yr (multiply lines #2 x #3 x #4 x #5 x #6 x #7)			___	___	___	___	___	___	___	___	___

* Critical input values

** Scaling Factor determined for Lines 2-5 from Appendix H - Emission Rate Estimate from Table H-2 divided by Typical Emission Rate defined in Case 22 (see line 9).

TABLE S-7
EMISSION RATE ESTIMATION WORKSHEET - OIL FILM SURFACE ON LAND TREATMENT UNIT

Line	Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12
	Modeling Parameters	Instruction A: Input Unit-Specific Values	Instruction B: Select a Representative Case from Appendix I - Table I-1 (underline selected case)	Instruction C: Determine Surrogate-Specific Scaling Factors**								
				HVHB	HVMB	HVLB	MVHB	MVMB	MVLB	LVMB	VHVHB	VHVLB
1	Area*	____ acres	--	--	--	--	--	--	--	--	--	--
2	Depth of Oil Film*	____ m	1,2,3 or 4	____	____	____	____	____	____	____	____	____
3	Applications per Year	____ /year	5, 6, 7 or 8	____	____	____	____	____	____	____	____	____
4	Constituent Concentration*	____ ppm	--	--	--	--	--	--	--	--	--	--
	INSTRUCTION D: Complete Lines 5-6 and 8			SURROGATE-SPECIFIC VALUES								
5	Account for Area [unit-specific area/(Case 18 area = 6.2 acres)]			____	____	____	____	____	____	____	____	____
6	Account for Concentration [unit-specific conc./(Case 18 conc. = 200 ppm)]			____	____	____	____	____	____	____	____	____
7	Typical Surrogate-Specific Emission Rate (Case 18), 10^6 g/yr			131.4	131.4	131.4	30.8	22.0	31.2	1.45E-03	131.4	131.4
8	Calculate Unit-Specific Emission Rate, 10^6 g/yr (multiply lines #2 x #3 x #5 x #6 x #7)			____	____	____	____	____	____	____	____	____

* Critical input values
** Scaling Factor determined for Lines 2 and 3 from Appendix I - Emission Rate Estimate from Table I-2 divided by Typical Emission Rate defined in Case 18 (see line 7).

TABLE S-8
EMISSION RATE ESTIMATION WORKSHEET - CLOSED LANDFILL

Line	Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12
	Modeling Parameters	Instruction A: Input Unit-Specific Values	Instruction B: Select a Representative Case from Appendix J - Table J-1 (underline selected case)	Instruction C. Determine Surrogate-Specific Scaling Factors**								
				HVHB	HVMB	HVLB	MVHB	MVMB	MVLB	LVMB	VHVHB	VHVLB
1	Area*	___ acres	--	--	--	--	--	--	--	--	--	--
2	Waste-bed thickness*	___ ft	1,2,3 or 4	___	___	___	___	___	___	___	___	___
3	Cap thickness	___ ft	5, 6, 7 or 8	___	___	___	___	___	___	___	___	___
4	Constituent content of waste*	___ percent	9, 10, 11 or 12	___	___	___	___	___	___	___	___	___
5	Air porosity	___ percent	13, 14, 15 or 16	___	___	___	___	___	___	___	___	___
	INSTRUCTION D: Complete Lines 6 and 8			SURROGATE-SPECIFIC VALUES								
6	Account for Area [unit-specific area/(Case 22 area = 3.5 acres)]			___	___	___	___	___	___	___	___	___
7	Typical Surrogate-Specific Emission Rate (Case 22), 10^6 g/yr			24.4	22.4	47.0	0.445	0.398	0.808	1.55E-05	119	264
8	Calculate Unit-Specific Emission Rate, 10^6 g/yr (multiply lines #2 x #3 x #4 x #5 x #6 x #7)			___	___	___	___	___	___	___	___	___

* Critical input values

** Scaling Factor determined for Lines 2-5 from Appendix J - Emission Rate Estimate from Table J-2 divided by Typical Emission Rate defined in Case 22 (see line 7).

TABLE S-9
EMISSION RATE ESTIMATION WORKSHEET - OPEN LANDFILL

Line	Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12
	Modeling Parameters	Instruction A: Input Unit-Specific Values	Instruction B: Select a Representative Case from Appendix K - Table K-1 (underline selected case)	Instruction C: Determine Surrogate-Specific Scaling Factors**								
				HVHB	HVMB	HVLB	MVHB	MVMB	MVLB	LVMB	VHVHB	VHVLB
1	Area*	____ acres	--	--	--	--	--	--	--	--	--	--
2	Waste-bed thickness*	____ ft	1,2,3 or 4	____	____	____	____	____	____	____	____	____
3	Constituent content of waste*	____ percent	5, 6, 7 or 8	____	____	____	____	____	____	____	____	____
4	Air porosity (fixed waste)	____ percent	9, 10, 11 or 12	____	____	____	____	____	____	____	____	____
5	Total porosity (fixed waste)	____ percent	13, 14, 15 or 16	____	____	____	____	____	____	____	____	____
	INSTRUCTION D: Complete Lines 6 and 8			SURROGATE-SPECIFIC VALUES								
6	Account for Area [unit-specific area/(Case 22 area = 3.5 acres)]			____	____	____	____	____	____	____	____	____
7	Typical Surrogate-Specific Emission Rate (Case 22), 10^6 g/yr			766.2	841.3	811.3	75.1	60.1	75.1	0.6	2358.7	2509.0
8	Calculate Unit-Specific Emission Rate, 10^6 g/yr (multiply lines #2 x #3 x #4 x #5 x #6 x #7)			____	____	____	____	____	____	____	____	____

* Critical input values

** Scaling Factor determined for Lines 2-5 from Appendix K - Emission Rate Estimate from Table K-2 divided by Typical Emission Rate defined in Case 22 (see line 7).

TABLE S-10
EMISSION RATE ESTIMATION WORKSHEET - WASTEPILES

Line	Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12
	Modeling Parameters	Instruction A: Input Unit-Specific Values	Instruction B: Select a Representative Case from Appendix L - Table L-1 (underline selected case)	Instruction C: Determine Surrogate-Specific Scaling Factors**								
				HVHB	HVMB	HVLB	MVHB	MVMB	MVLB	LVMB	VHVHB	VHVLB
1	Area*	___ acres	--	--	--	--	--	--	--	--	--	--
2	Turnover rate*	___ per year	1, 2, 3 or 4	___	___	___	___	___	___	___	___	___
3	Constituent content of waste*	___ percent	5, 6, 7 or 8	___	___	___	___	___	___	___	___	___
4	Air porosity (fixed waste)	___ percent	9, 10, 11 or 12	___	___	___	___	___	___	___	___	___
5	Total porosity (fixed waste)	___ percent	13, 14, 15 or 16	___	___	___	___	___	___	___	___	___
	INSTRUCTION D: Complete Lines 6 and 8			SURROGATE-SPECIFIC VALUES								
6	Account for Area [unit-specific area/(Case 22 area = 0.1 acres)]			___	___	___	___	___	___	___	___	___
7	Typical Surrogate-Specific Emission Rate (Case 22), 10^6g/yr			261.4	284.9	277.0	26.0	20.9	25.5	0.2	799.3	852.1
8	Calculate Unit-Specific Emission Rate, 10^6g/yr (multiply lines #2 x #3 x #4 x #5 x #6 x #7)			___	___	___	___	___	___	___	___	___

* Critical input values

** Scaling Factor determined for Lines 2-5 from Appendix L - Emission Rate Estimate from Table L-2 divided by Typical Emission Rate defined in Case 22 (see line 7).

TABLE S-11
EMISSION RATE ESTIMATION WORKSHEET - FIXED ROOF TANKS

Line	Col 1	Col 2	Col 3		Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12
	Modeling Parameters	Instruction A: Input Unit-Specific Values	Instuction B: Select a Representative Case from Appendix M - Table M-2 (underline selected case)		Instruction C: Determine Surrogate-Specific Scaling Factors**								
					HVHB	HVMB	HVLB	MVHB	MVMB	MVLB	LVMB	VHVHB	VHVLB
1	Diameter*	___ft	1, 2, 3, 4, 5 or 6	Breathing Loss	___	___	___	___	___	___	___	___	___
2				Working Loss	___	___	___	___	___	___	___	___	___
3	Height*	___ft	7, 8, 9, 10 or 11	Breathing Loss	___	___	___	___	___	___	___	___	___
4				Working Loss	___	___	___	___	___	___	___	___	___
5	Throughput*	___x10^6 gal/yr	12, 13, 14, 15, 16 or 17	Working Loss	___	___	___	___	___	___	___	___	___

	INSTRUCTION D: Complete Lines 8-10	SURROGATE-SPECIFIC VALUES								
6	Typical Surrogate-Specific Working Loss Emission Rate (Case 23), 10^6 g/yr	---	---	---	3.9	3.5	7.1	0.0001	---	---
7	Typical Surrogate-Specific Breathing Loss Emission Rate (Case 23), 10^6 g/yr	---	---	---	1.8	1.8	3.2	0.0015	---	---
8	Calculate Unit-Specific Working Loss Emission Rate, 10^6 g/yr (multiply Lines #2 x #4 x #5 x #6)	___	___	___	___	___	___	___	___	___
9	Calculate Unit-Specific Breathing Loss Emission Rate, 10^6 g/yr (multiply Lines #1 x #3 x #7)	___	___	___	___	___	___	___	___	___
10	Calculate Total Emission Rate, 10^6 g/yr (add Lines #8 + #9)	___	___	___	___	___	___	___	___	___

* Critical input values

** Scaling Factor determined for Lines 1-5 from Appendix M - Emission Rate Estimate from Table M-2 divided by Typical Emission Rate defined in Case 23 (see lines 7 and 8).

TABLE S-12
EMISSION RATE ESTIMATION WORKSHEET - FLOATING ROOF TANKS

Line	Col 1	Col 2	Col 3		Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12
	Modeling Parameters	Instruction A: Input Unit-Specific Values	Instuction B: Select a Representative Case from Appendix N - Table N-1 (underline selected case)		Instruction C: Determine Surrogate-Specific Scaling Factors**								
					HVHB	HVMB	HVLB	MVHB	MVMB	MVLB	LVMB	VHVHB	VHVLB
1	Rim seal class*	___	1, 2, 3, 4, 5, 6, 7 or 8	Rim Loss	___	___	___	___	___	___	___	___	___
2	Shell type*	___	9, 10 or 11	Withdrawal Loss	___	___	___	___	___	___	___	___	___
3	Average liquid density*	___ lb/gal	12, 13, 14, 15 or 16	Withdrawal Loss	___	___	___	___	___	___	___	___	___
4	Diameter*	___ ft	17, 18, 19, 20 or 21	RIM Loss	___	___	___	___	___	___	___	___	___
5				Withdrawal Loss	___	___	___	___	___	___	___	___	___
6				Fitting Loss	___	___	___	___	___	___	___	___	___
7	Throughput	___ x10^6 gal/yr	---		---	---	---	---	---	---	---	---	---

	INSTRUCTION D: Complete Lines 8 and 12-15	SURROGATE-SPECIFIC VALUES								
8	Account for Throughput [unit-specific throughput/(Case 27 throughput = 63x10^6 gal/yr)]	___	___	___	___	___	___	___	___	___
9	Typical Surrogate-Specific Rim Loss Emission Rate (Case 27), 10^6 g/yr	---	---	---	1.0	0.95	1.9	0.00004	---	---
10	Typical Surrogate-Specific Withdrawal Loss Emission Rate (Case 27), 10^6 g/yr	---	---	---	0.062	0.062	0.062	0.062	---	---
11	Typical Surrogate-Specific Fitting Loss Emission Rate (Case 27), 10^6 g/yr	---	---	---	0.030	0.028	0.056	0.000001	---	---
12	Calculate Unit-Specific Rim Loss Emission Rate, 10^6 g/yr (multiply lines #1 x #4 x #9)	___	___	___	___	___	___	___	___	___
13	Calculate Unit-Specific Withdrawal Loss Emission Rate, 10^{6}g/yr (multiply lines #2 x #3 x #5 x #8x #10)	___	___	___	___	___	___	___	___	___
14	Calculate Unit-Specific Fitting Loss Emission Rate, 10^{6}g/yr (multiply lines #6 x #11)	___	___	___	___	___	___	___	___	___
15	Calculate Total Emission Rate, 10^{6}g/yr (add lines #12 + #13 + #14)	___	___	___	___	___	___	___	___	___

* Critical input values

** Scaling Factor determined for Lines 1-6 from Appendix N - Emission Rate Estimate from Table N-2 divided by Typical Emission Rate defined in Case 27 (see lines 10 and 11).

TABLE S-13
EMISSION RATE ESTIMATION WORKSHEET - VARIABLE VAPOR SPACE TANKS

Line	Col 1	Col 2	Col 3	Col 4	Col 5	Col 6	Col 7	Col 8	Col 9	Col 10	Col 11	Col 12
	Modeling Parameters	Instruction A: Input Unit-Specific Values	Instruction B: Select a Representative Case from Appendix O - Table O-1 (underline selected case)	Instruction C: Determine Surrogate-Specific Scaling Factors**								
				HVHB	HVMB	HVLB	MVHB	MVMB	MVLB	LVMB	VHVHB	VHVLB
1	Throughput*	___ x10^{6}gal/yr	1,2,3 or 4	___	___	___	___	___	___	___	___	___
2	Transfers into tank*	___ #/yr	5, 6, 7 or 8	___	___	___	___	___	___	___	___	___
		INSTRUCTION D: Complete Line 4		SURROGATE-SPECIFIC VALUES								
3	Typical Surrogate-Specific Emission Rate (Case 14) 10^{6}g/yr			30	26	59	0.57	0.53	1.1	1.9E-05	150	320
4'	Calculate Unit-Specific Emission Rate, 10^6 g/yr (multiply Lines #1 x #2 x #3)			___	___	___	___	___	___	___	___	___

* Critical input values

** Scaling Factor determined for Lines 1 and 2 from Appendix O - Emission Rate Estimate from Table O-2 divided by Typical Emission Rate defined in Case 14 (see line 3).

TABLE S-14
EMISSION RATE ESTIMATION WORKSHEET - PARTICLES FROM STORAGE PILES

Col 1		Col 2	Col 3		Col 4
Line	Modeling Parameters	Instruction A: Input Unit - Specific Values	Instruction B: Select a Representative Case from Appendix P - Table P-1 (underline selected case)		Instruction C: Determine Scaling Factor **
1	Area	_____ acres	---		-----
2	Silt content*	_____ %	1, 2, 3 or 4	wind erosion	_____
3	Silt content*			batch dump	_____
4	Silt content*			vehicle activity	_____
5	% of time wind speed exceeds 12 mph*	_____ %	5, 6, 7 or 8	wind erosion	_____
6	Days precipitation	_____ days	9, 10, 11 or 12	wind erosion	_____
	(≥ .01 inch/day)			vehicle activity	_____
7	Mean wind speed*	_____ mph	13, 14 or 15	batch dump	_____
8	Moisture content*	_____ %	16, 17, 18 or 19	batch dump	_____
9	Vehicle weight*	_____ tons	20, 21 or 22	vehicle activity	_____
10	Vehicle wheels*	_____ #	---		_____
11	Throughput*	_____ tons/yr	---		_____
12	Mass fraction of contaminant	_____ ppm	---		_____

	INSTRUCTION D: Complete Lines 13-15 and 19-22	SURROGATE-SPECIFIC VALUES
13	Account for Area [unit-specific area/(Case 28 area = 5 acres)]	_____
14	Account for Vehicle Wheels [square root (vehicle wheels)/square root (Case 28 wheels = $\sqrt{4}$)]	_____
15	Account for Throughput [unit throughput/(Case 28 throughput = 50,000 tons/yr)]	_____
16	Typical case emission rate - wind erosion (Case 28), 10^6 g/yr	6.2×10^{-6}
17	Typical case emission rate - batch dump (Case 28), 10^6 g/yr	8.7×10^{-6}
18	Typical case emission rate - vehicle activity (Case 28), 10^6 g/yr	1.1×10^{-6}
19	Calculate Unit-Specific Emission Rate - Wind Erosion, 10^6 g/yr (multiply lines #2 x #5 x #6 x #13 x #16)	_____
20	Calculate Unit-Specific Emission Rate - Batch Dump, 10^6 g/yr (multiply lines #3 x #7 x #8 x #15 x #17)	_____
21	Calculate Unit-Specific Emission Rate - Vehicle Activity, 10^6 g/yr (multiply lines #4 x #7 x #9 x #14 x #18)	_____
22	Calculate Total Emission Rate, 10^6 g/yr (add lines #19 + #20 + #21)	_____

* Critical input value

** Scaling factor determined for Lines 2-12 from Appendix P - Emission Rate Estimate from Table P-2 divided by Typical Emission Rate defined in Case 28 (see lines 16, 17, and 18).

TABLE S-15
EMISSION RATE ESTIMATION WORKSHEET - PARTICLES FROM EXPOSED, FLAT, CONTAMINATED AREAS

Line	Col 1	Col 2	Col 3	Col 4
	Modeling Parameters	Instruction A: Input Unit-Specific Values	Instruction B: Select Representative Case from Appendix Q - Table Q-1 (underline selected case)	Instruction C: Determine Scaling Factor**
1	Area*	____acres	--	--
2	Silt Content*	____%	1, 2, 3 or 4	_____
3	Surface erodibility*	____tons/acre-year	5, 6, 7, 8 or 9	_____
4	% of time windspeed >12 mph*	____%	15, 16, 17 or 18	_____
5	Mass fraction of contaminant*	____ppm	--	--
6	$100^2/(\text{PE index})^2$	____	--	--

	INSTRUCTION D: Complete Lines 7-8 and 10	SURROGATE-SPECIFIC VALUES
7	Account for Unit-Specific Area [unit-specific area/(Case 24 area = 5 acres)]	_____
8	Account for Mass Fraction of Contaminant [unit-specific mass fraction/(Case 24 mass fraction = 1 ppm)]	_____
9	Typical Case Emission Rate (Case 24), 10^6 g/yr	3.6×10^{-7}
9	Calculate Unit-Specific Emission Rate, 10^6 g/yr (multiply line #2 x #3 x #4 x #6 x #7 x #8 x #9)	_____

* Critical input values

** Scaling Factor determined for Lines 2-4 from Appendix Q - Emission Rate Estimate from Table Q-2 divided by Typical Emission Rate defined in Case 24 (see line 9)

APPENDIX H

SOIL LOSS CALCULATION

EXCERPTED FROM

U.S. EPA. Final Draft Superfund Exposure Assessment Manual. September, 1987. Office of Emergency and Remedial Response, Washington, D.C. 20460

APPENDIX H

SOIL LOSS CALCULATION

Introduction

Many of the organic substances of concern found at Superfund sites are relatively nonpolar, hydrophobic substances (Delos et al., 1984). Such substances can be expected to sorb to site soils and migrate from the site more slowly than will polar compounds. As discussed in Haith (1980) and Mills et al. (1982), estimates of the amount of hydrophobic compounds released in site runoff can be calculated using the Modified Universal Soil Loss Equation (MUSLE) and sorption partition coefficients derived from the compound's octanol-water partition coefficient. The MUSLE allows estimation of the amount of surface soil eroded in a storm event of given intensity, while sorption coefficients allow the projection of the amounts of contaminant carried along with the soil, and the amount carried in dissolved form.

Soil Loss Calculation

Equation 2-20 is the basic equation for estimating soil loss. Equations 2-21 through 2-24 are used to calculate certain input parameters required to apply Equation 2-20. The modified universal soil loss equation (Williams 1975), as presented in Mills et al. (1982), is:

$$Y(S)_E = a(V_r q_p)^{0.56}\,KLSCP \qquad (2\text{-}20)$$

where

$Y(s)_E$	=	sediment yield (tons per event, metric tons per event).
a	=	conversion constant, (95 English, 11.8 metric).*
V_r	=	volume of runoff, (acre-feet, m^3).
q_p	=	peak flow rate, (cubic feet per second, m^3/sec).

* Metric conversions presented in the following runoff contamination equations are from Mills et al. (1982).

K	=	the soil erodibility factor, (commonly expressed in tons per acre per dimensionless rainfall erodibility unit). K can be obtained from the local Soil Conservation Service office.
L	=	the slope-length factor, (dimensionless ratio).
S	=	the slope-steepness factor, (dimensionless ratio).
C	=	the cover factor, (dimensionless ratio: 1.0 for bare soil); see the following discussion for vegetated site "C" values).
P	=	the erosion control practice factor, (dimensionless ratio: 1.0 for uncontrolled hazardous waste sites).

Soil erodibility factors are indicators of the erosion potential of given soils types. As such, they are highly site-specific. K values for sites under study can be obtained from the local Soil Conservation Service office. The slope length factor, L, and the slope steepness factor, S, are generally entered into the MUSLE as a combined factor, LS, which is obtained from Figures 2-4 through 2-6. The cover management factor, C, is determined by the amount and type of vegetative cover present at the site. Its value is "1" (one) for bare soils. Consult Tables 2-4 through 2-5 to obtain C values for sites with vegetative covers. The factor, P, refers to any erosion control practices used on-site. Because these generally describe the type of agricultural plowing or planting practices, and because it is unlikely that any erosion control would be practiced at an abandoned hazardous waste site, use a worst-case (conservative) P value of 1 (one) for uncontrolled sites.

Storm runoff volume, V_r, is calculated as follows (Mills et al. 1982):

$$V_r = aAQ_r \qquad (2\text{-}21)$$

where

a	=	conversion constant, (0.083 English, 100 metric).
A	=	contaminated area, (acres, ha).
Q_r	=	depth of runoff, (in, cm).

Depth of runoff, Q_r, is determined by (Mockus 1972):

$$Q_r = (R_t - 0.2S_w)^2/(R_t + 0.8S_w) \qquad (2\text{-}22)$$

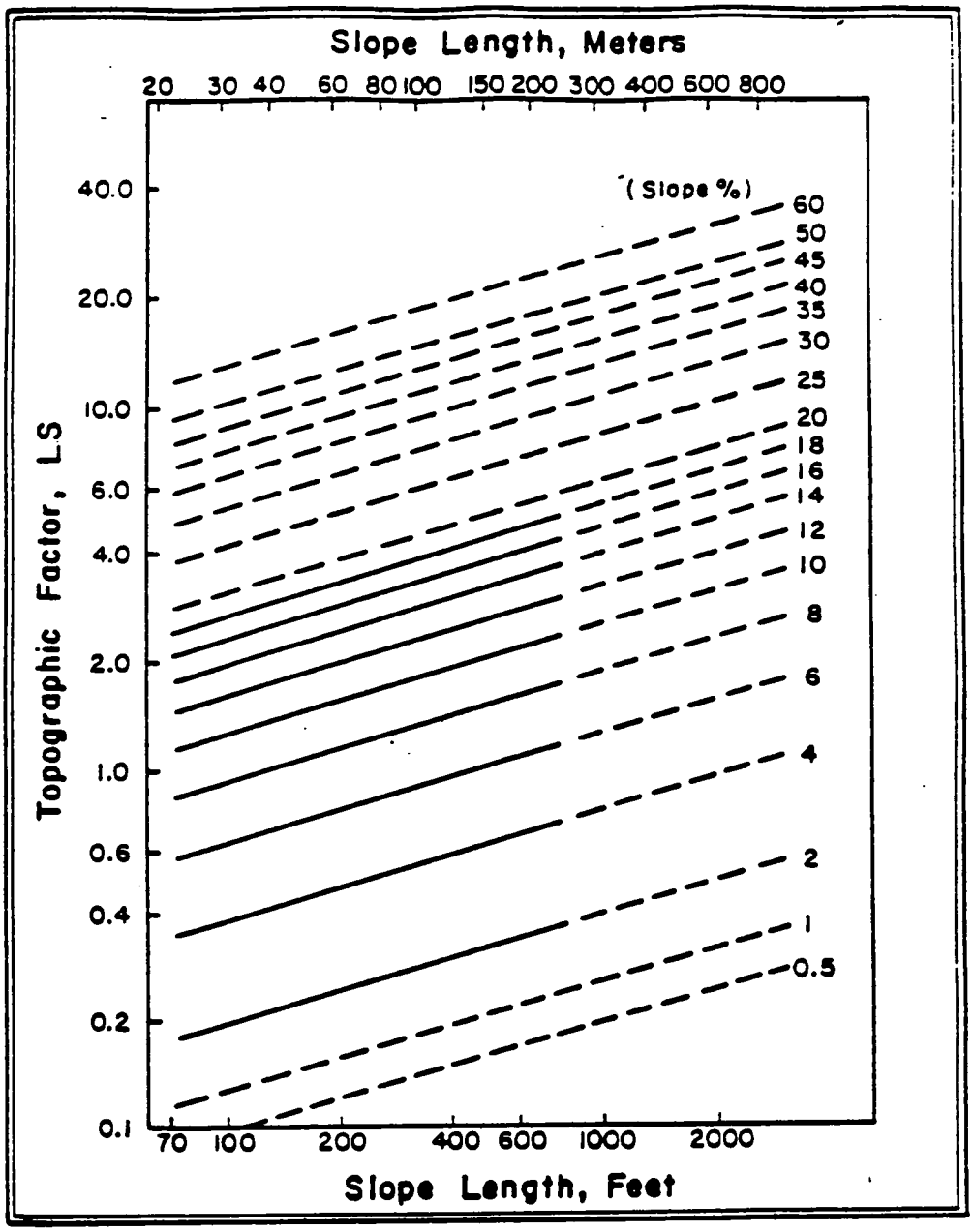

Figure 2-4. Slope Effect chart Applicable to Areas A-1 in Washington, Oregon, and Idaho, and All of A-3: See Figure 3-5 (USDA 1974 as Presented in Mills et al. 1982).

NOTE: Dashed lines are extension of LS formulae beyond values tested in studies.

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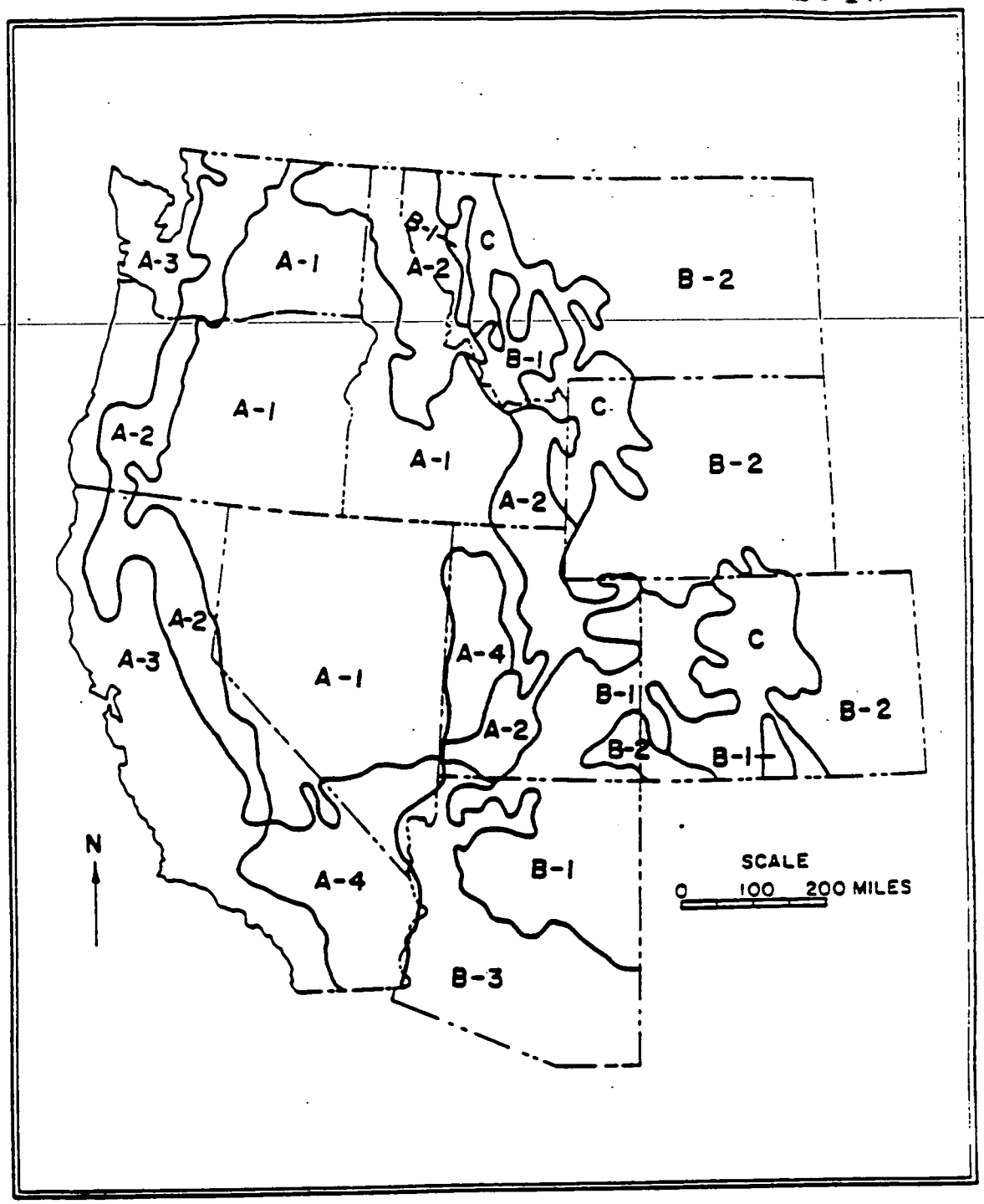

Figure 2-5. Soil Moisture-Soil Temperature Regimes of the Western United States (USDA 1974).

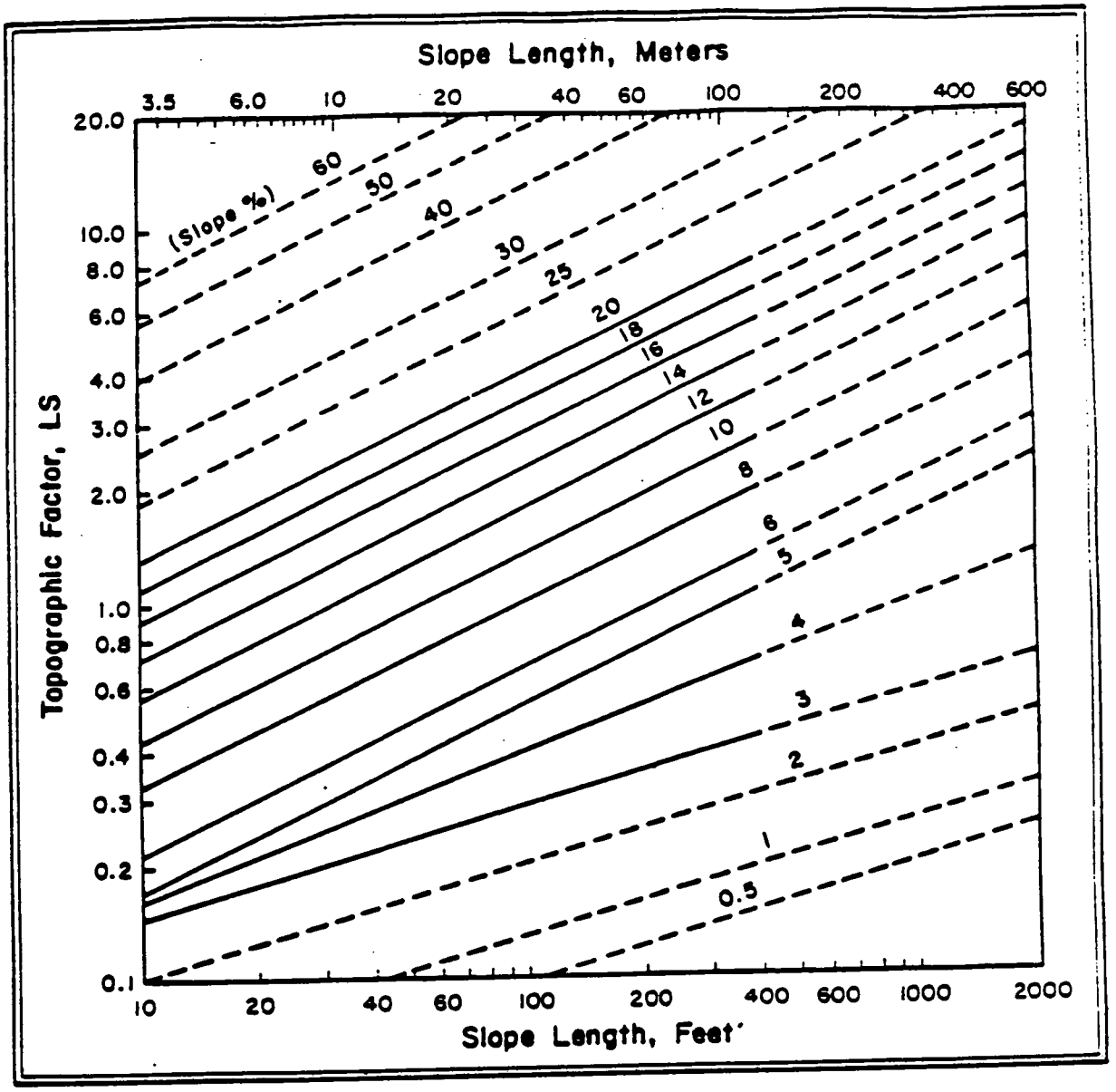

Figure 2-6. Slope Effect Chart for Areas Where Figure 3-5 Is Not Applicable (USDA 1974).

NOTE: The dashed lines represent estimates for slope dimensions beyond the range of lengths and steepnesses for which data are available.

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TABLE 2-4

"C" VALUES FOR PERMANENT PASTURE, RANGELAND, AND IDLE LAND

Vegetal canopy Type and height of raised canopy[b]	Canopy cover[c] (%)	Cover that contacts the surface/Percent groundcover						
		Type[d]	0	20	40	60	80	95-100
No appreciable canopy		G	0.45	0.20	0.10	0.042	0.013	0.003
		W	0.45	0.24	0.15	0.090	0.043	0.011
Canopy of tall weeds or short brush (0.5 m fall height)	25	G	0.36	0.17	0.09	0.038	0.012	0.003
		W	0.36	0.20	0.13	0.082	0.041	0.011
	50	G	0.26	0.13	0.07	0.035	0.012	0.003
		W	0.26	0.16	0.11	0.075	0.039	0.011
	75	G	0.17	0.10	0.06	0.031	0.011	0.003
		W	0.17	0.12	0.09	0.067	0.038	0.011
Appreciable brush or brushes (2 m fall height)	25	G	0.40	0.18	0.09	0.040	0.013	0.003
		W	0.40	0.22	0.14	0.085	0.042	0.011
	50	G	0.34	0.16	0.085	0.038	0.012	0.003
		W	0.34	0.19	0.13	0.081	0.041	0.011
	75	G	0.28	0.14	0.08	0.036	0.012	0.003
		W	0.28	0.17	0.12	0.077	0.040	0.011
Trees but no appreciable low brush (4 m fall height)	25	G	0.42	0.19	0.10	0.041	0.013	0.003
		W	0.42	0.23	0.14	0.087	0.042	0.011
	50	G	0.39	0.18	0.09	0.040	0.013	0.003
		W	0.39	0.21	0.14	0.085	0.042	0.011
	75	G	0.36	0.17	0.09	0.039	0.012	0.003
		W	0.36	0.20	0.13	0.083	0.041	0.011

Source: Wischemier 1972.

[a] All values shown assume: (1) random distribution of mulch or vegetation and (2) mulch of appreciable depth where it exists.

[b] Average fall height of waterdrops from canopy to soil surface: m = meters.

[c] Portion of total-area surface that would be hidden from view by canopy in a vertical projection (a bird's-eye view).

[d] G: Cover at surface is grass, grasslike plants, decaying compacted duff, or litter at least 5 cm (2 in.) deep.
W: Cover at surface is mostly broadleaf herbaceous plants (as weeds) with little laterial-root network near the surface and/or undecayed residue.

TABLE 2-5

"C" VALUES FOR WOODLAND

Stand condition	Tree canopy percent of area[a]	Forest litter percent of area[b]	Undergrowth[c]	"C" factor
Well stocked	100-75	100-90	Managed[d] Unmanaged[d]	0.001 0.003-0.011
Medium stocked	70-40	85-75	Managed Unmanaged	0.002-0.004 0.01-0.04
Poorly stocked	35-20	70-40	Managed Unmanaged	0.003-0.009 0.02-0.09[e]

Source: Wischemier 1972.

a When tree canopy is less than 20 percent, the area will be considered as grass land or cropland for estimating soil loss.

b Forest litter is assumed to be at least 2 in. deep over the percent ground surface area covered.

c Undergrowth is defined as shrubs, weeds, grasses, vines, etc., on the surface area not protected by forest litter. Usually found under canopy openings.

d Managed - grazing and fires are controlled.
Unmanaged - stands that are overgrazed or subjected to repeated burning.

e For unmanaged woodland with litter cover of less than 75 percent, C values should be derived by taking 0.7 of the appropriate values in Table 3-4. The factor of 0.7 adjusts for much higher soil organic matter on permanent woodland.

where

R_t = the total storm rainfall, (in, cm).

S_w = water retention factor, (in, cm).

The value of S_w, the water retention factor, is obtained as follows (Mockus 1972):

$$S_w = \frac{1000}{CN} - 10\,a \qquad (2\text{-}23)$$

where

S_w = water retention factor, (in, cm).

CN = the SCS Runoff Curve Number, (dimensionless, see Table 2-6).

a = conversion constant (1.0 English, 2.54 metric).

The CN factor is determined by the type of soil at the site, its condition, and other parameters that establish a value indicative of the tendency of the soil to absorb and hold precipitation or to allow precipitation to run off the surface. The analyst can obtain CN values of uncontrolled hazardous waste sites from Table 2-6.

The peak runoff rate, q_p, is determined as follows (Haith 1980):

$$q_p = \frac{aAR_tQ_r}{T_r(R_t - 0.2S_w)} \qquad (2\text{-}24)$$

where

q_p = the peak runoff rate, (ft^3/sec, m^3/sec).

a = conversion constant, (1.01 English, 0.028 metric).

A = contaminated area, (acres, ha).

R_t = the total storm rainfall, (in, cm).

Q_r = the depth of runoff from the watershed area, (in, cm).

T_r = storm duration, (hr).

TABLE 2-6

RUNOFF CURVE NUMBERS

Soil Group	Description	Site Type			
		Overall site[a]	Road/right of way	Meadow	Woods
A	Lowest runoff potential: Includes deep sands with very little silt and clay, also deep, rapidly permeable loess (infiltration rate = 8-12 mm/h).	59	74	30	45
B	Moderately low runoff potential: Mostly sandy soils less deep than A, and loess less deep or less aggregated than A, but the group as a whole has above-average infiltration after thorough wetting (infiltration rate = 4-8 mm/h).	74	84	58	66
C	Moderately high runoff potential: Comprises shallow soils and soils containing considerable clay and colloids, though less than those of group D. The group has below-average infiltration after presaturation (infiltration rate = 1-4 mm/h).	82	90	71	77
D	Highest runoff potential: Includes mostly clays of high swelling percent, but the group also includes some shallow soils with nearly impermeable subhorizons near the surface (infiltration rate = 0-1 mm/h).	86	92	78	83

Source: Adapted from Schwab et al. 1966.

[a] Values taken from farmstead category, which is a composite including buildings, farmyard, road, etc.

S_w = water retention factor, (in, cm).

Dissolved/Sorbed Contaminant Release

As discussed in Mills et al. (1985), the analyst can predict the degree of soil/water partitioning expected for given compounds once the storm event soil loss has been calculated with the following equations. First, the amounts of absorbed and dissolved substances are determined, using the equations presented below as adapted from Haith (1980):

$$S_s = [1/(1 + \theta_c/K_d\beta)]\,(C_i)\,(A) \qquad (2\text{-}25)$$

and

$$D_s = [1/(1 + K_d\beta/\theta_c)]\,(C_i)\,(A) \qquad (2\text{-}26)$$

where

S_s = sorbed substance quantity, (kg, lb).

θ_c = available water capacity of the top cm of soil (difference between wilting point and field capacity), (dimensionless).

K_d = sorption partition coefficient, (cm^3/g).

β = soil bulk density, (g/cm^3).

C_i = total substance concentration, (kg/ha-cm, lb/acre-cm).

A = contaminated area, (ha-cm, acre-cm). (Actually a volume; assumption is contamination in upper 1 cm is available for release).

D_s = dissolved substance quantity, (kg, lb).

This model assumes that only the contaminant in the top 1 cm of soil is available for release via runoff.

The soil sorption partition coefficient for a given chemical can be determined from known values of certain other physical/chemical parameters, primarily the chemical's octanol-water partition coefficient, solubility in water, or bioconcentration factor. Lyman et al. (1982) present regression equations that allow the analyst to determine sorption coefficients for specified groups of chemicals (e.g., herbicides, polynuclear aromatics). If parameter values required by the appropriate equations are not available in chemical reference literature, they

can be estimated according to procedures described in Lyman et al. (1982). Initially, the octanol-water partition coefficient can be estimated based on the substance's molecular structure. If necessary, this value can be used, in turn, to estimate either solubility in water or bioconcentration factor.

After calculating the amount of sorbed and dissolved contaminant, the total loading to the receiving waterbody is calculated as follows (adapted from Haith 1980):

$$PX_i = [Y(S)_E/100\ \beta]\ S_s \qquad (2\text{-}27)$$

and

$$PQ_i = [Q_r/R_t]\ D_s \qquad (2\text{-}28)$$

where

Px_i	=	sorbed substance loss per event, (kg, lb).
$Y(S)_E$	=	sediment yield, (tons per event, metric tons).
β	=	soil bulk density, (g/cm^3).
S_s	=	sorbed substance quantity, (kg, lb).
PQ_i	=	dissolved substance loss per event, (kg, lb).
Q_r	=	total storm runoff depth, (in, cm).
R_t	=	total storm rainfall, (in, cm).
D_s	=	dissolved substance quantity, (kg, lb).

Px_i and PQ_i can be converted to mass per volume terms for use in estimating contaminant concentration in the receiving waterbody by dividing by the site storm runoff volume (V_r, see Equation 2-21).

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INTERIM FINAL

RCRA FACILITY INVESTIGATION (RFI) GUIDANCE

VOLUME IV OF IV

CASE STUDY EXAMPLES

EPA 530/SW-89-031

MAY 1989

WASTE MANAGEMENT DIVISION
OFFICE OF SOLID WASTE
U.S. ENVIRONMENTAL PROTECTION AGENCY

ABSTRACT

On November 8, 1984, Congress enacted the Hazardous and Solid Waste Amendments (HSWA) to RCRA. Among the most significant provisions of HSWA are §3004(u), which requires corrective action for releases of hazardous waste or constituents from solid waste management units at hazardous waste treatment, storage and disposal facilities seeking final RCRA permits; and §3004(v), which compels corrective action for releases that have migrated beyond the facility property boundary. EPA will be promulgating rules to implement the corrective action provisions of HSWA, including requirements for release investigations and corrective measures.

This document, which is presented in four volumes, provides guidance to regulatory agency personnel on overseeing owners or operators of hazardous waste management facilities in the conduct of the second phase of the RCRA Corrective Action Program, the RCRA Facility Investigation (RFI). Guidance is provided for the development and performance of an investigation by the facility owner or operator based on determinations made by the regulatory agency as expressed in the schedule of a permit or in an enforcement order issued under §3008(h), §7003, and/or §3013. The purpose of the RFI is to obtain information to fully characterize the nature, extent and rate of migration of releases of hazardous waste or constituents and to interpret this information to determine whether interim corrective measures and/or a Corrective Measures Study may be necessary.

DISCLAIMER

This document is intended to assist Regional and State personnel in exercising the discretion conferred by regulation in developing requirements for the conduct of RCRA Facility Investigations (RFIs) pursuant to 40 CFR 264. Conformance with this guidance is expected to result in the development of RFIs that meet the regulatory standard of adequately detecting and characterizing the nature and extent of releases. However, EPA will not necessarily limit acceptable RFIs to those that comport with the guidance set forth herein. This document is not a regulation (i.e., it does not establish a standard of conduct which has the force of law) and should not be used as such. Regional and State personnel must exercise their discretion in using this guidance document as well as other relevant information in determining whether an RFI meets the regulatory standard.

Mention of company or product names in this document should not be considered as an endorsement by the U.S. Environmental Protection Agency.

RCRA FACILITY INVESTIATION (RFI) GUIDANCE

VOLUME IV

CASE STUDY EXAMPLES

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LIST OF ACRONYMS

AA	-	Atomic Absorption
AI	-	Soil Adsorption Isotherm Test
ASCS	-	Agricultural Stabilization and Conservation Service
ASTM	-	American Society for Testing and Materials
BCF	-	Bioconcentration Factor
BOD	-	Biological Oxygen Demand
CAG	-	EPA Carcinogen Assessment Group
CPF	-	Carcinogen Potency Factor
CBI	-	Confidential Business Information
CEC	-	Cation Exchange Capacity
CERCLA	-	Comprehensive Environmental Response, Compensation, and Lability Act
CFR	-	Code of Federal Regulations
CIR	-	Color Infrared
CM	-	Corrective Measures
CMI	-	Corrective Measures Implementation
CMS	-	Corrective Measures Study
COD	-	Chemical Oxygen Demand
COLIWASA	-	Composite Liquid Waste Sampler
DNPH	-	Dinitrophenyl Hydrazine
DO	-	Dissolved Oxygen
DOT	-	Department of Transportation
ECD	-	Electron Capture Detector
EM	-	Electromagnetic
EP	-	Extraction Procedure
EPA	-	Environmental Protection Agency
FEMA	-	Federal Emergency Management Agency
FID	-	Flame Ionization Detector
Foc	-	Fraction organic carbon in soil
FWS	-	U.S. Fish and Wildlife Service
GC	-	Gas Chromatography
GC/MS	-	Gas Chromatography/Mass Spectroscopy
GPR	-	Ground Penetrating Radar
HEA	-	Health and Environmental Assessment
HEEP	-	Health and Environmental Effects Profile
HPLC	-	High Pressure Liquid Chromatography
HSWA	-	Hazardous and Solid Waste Amendments (to RCRA)
HWM	-	Hazardous Waste Management
ICP	-	Inductively Coupled (Argon) Plasma
ID	-	Infrared Detector
Kd	-	Soil/Water Partition Coefficient
Koc	-	Organic Carbon Absorption Coefficient
Kow	-	Octanol/Water Partition Coefficient
LEL	-	Lower Explosive Limit
MCL	-	Maximum Contaminant Level
MM5	-	Modified Method 5
MS/MS	-	Mass Spectroscopy/Mass Spectroscopy
NFIP	-	National Flood Insurance Program
NIOSH	-	National Institute for Occupational Safety and Health

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LIST OF ACRONYMS (Continued)

NPDES	-	National Pollutant Discharge Elimination System
OSHA	-	Occupational Safety and Health Administration
OVA	-	Organic Vapor Analyzer
PID	-	Photo Ionization Detector
pKa	-	Acid Dissociation Constant
ppb	-	parts per billion
ppm	-	parts per million
PUF	-	Polyurethane Foam
PVC	-	Polyvinyl Chloride
QA/QC	-	Quality Assurance/Quality Control
RCRA	-	Resource Conservation and Recovery Act
RFA	-	RCRA Facility Assessment
RfD	-	Reference Dose
RFI	-	RCRA Facility Investigation
RMCL	-	Recommended Maximum Contaminant Level
RSD	-	Risk Specific Dose
SASS	-	Source Assessment Sampling System
SCBA	-	Self Contained Breathing Apparatus
SCS	-	Soil Conservation Service
SOP	-	Standard Operating Procedure
SWMU	-	Solid Waste Management Unit
TCLP	-	Toxicity Characteristic Leaching Procedure
TEGD	-	Technical Enforcement Guidance Document (EPA, 1986)
TOC	-	Total Organic Carbon
TOT	-	Time of travel
TOX	-	Total Organic Halogen
USGS	-	United States Geologic Survey
USLE	-	Universal Soil Loss Equation
UV	-	Ultraviolet
VOST	-	Volatile Organic Sampling Train
VSP	-	Verticle Seismic Profiling
WQC	-	Water Quality Criteria

14.0 INTRODUCTION

14.1 Use of Case Studies

This document, Volume IV of the RCRA Facility Investigation (RFI) Guidance, contains case studies selected to illustrate various concepts and procedures presented in Volumes I, II, and III. These case studies are provided to explain, through example, how various tasks can be conducted during RFIs. The case studies also identify some of the potential problems that can occur if the RFI sampling and analytical programs are not carefully designed and executed. The case studies, however, should not be used as the primary source of guidance for RFI program design and conduct. Instead, Volumes I, II and III should be consulted. The studies do not necessarily address details specific to individual facilities, and omission of certain RFI tasks should not be interpreted as an indication that such tasks are unnecessary or of less significance. Most of the case studies are based on actual sites. In some cases, existing data have been supplemented with hypothetical data to illustrate a particular point.

14.2 Organization of Volume IV

The case studies are organized primarily by the order in which the subject matter was presented in Volumes I, II and III. In some cases, individual case studies present materials relevant to more than one topic or media. Table 14-1 lists the points illustrated and identifies the case studies which provide information relevant to these points.

The following general format was used as appropriate for each case study:

- Title
- Identification of points illustrated
- Introduction/Background
- Facility description
- Program design/Data collection
- Program results/Data analysis
- Case discussion.

TABLE 14-1

SUMMARY OF POINTS ILLUSTRATED

POINTS ILLUSTRATED	CASE STUDY NUMBER
SELECTION OF MONITORING CONSTITUENTS	
• Use of 40 CFR Part 261 Listing Background Documents in selecting monitoring constituents	1
• Consideration of degradation as a factor in identifying monitoring constituents	2
SAMPLING SCHEMES	
• Selection of a sampling scheme that appropriately characterizes soil contamination	3
• Evaluation of the effectiveness of a sampling scheme using statistical analyses	3
• Use of release monitoring/leachate collection to characterize wastes when the actual waste stream is inaccessible, as in the case of buried drums	4
QUALITY ASSURANCE AND CONTROL	
• Use of quality assurance and control and data validation procedures	5
DATA PRESENTATION	
• Techniques for presenting data for facility investigations involving multimedia contamination	6
WASTE CHARACTERIZATION	
• Correlation of a contaminant release with a specific waste management unit using ground-water data	7
• Use of site topographic information to select test boring and monitoring well locations at facilities where large volumes of waste have been disposed	8
• Use of waste stream information to select indicator parameters and monitoring constituents in a ground-water monitoring program to minimize the number of constituents that must be monitored	9
• Use of information on possible waste reaction products in designing a ground-water monitoring program	10
CORRECTIVE MEASURES INCLUDING INTERIM MEASURES	
• Use of biodegradation and removal for interim corrective measures	2
• Corrective action and the implementation of interim corrective measures	11
AERIAL PHOTOGRAPHY	
• Use of aerial photographs to identify actual and potential waste migration routes and areas requiring corrective action	12
• Identification of a ground-water contaminant plume using infrared aerial photography	13
• Use of historical aerial photographs and facility maps to identify old waste disposal areas and ground-water flow paths	14

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TABLE 14-1

SUMMARY OF POINTS ILLUSTRATED (continued)

POINTS ILLUSTRATED	CASE STUDY NUMBER
SOIL	
• Use of soil characteristics to estimate mobility of contaminants in soil	15
• Effects of degradation in determining the fate of a contaminant in soil	2
• Use of leaching tests to predict potential impacts of contaminated soils on ground water	16
GROUND WATER	
• Use of split-spoon sampling and organic vapor monitoring to select screened intervals for ground-water monitoring	17
• Development of a two-phase boring program to investigate ground-water contamination	18
• Use of basement monitoring to estimate contaminant migration	19
• Use of mathematical models to determine locations of ground-water monitoring wells	20
• Monitoring and characterization of ground-water contamination when two liquid phases are present	21
• Methodology for construction of vertical flow nets	22
SUBSURFACE GAS	
• Design of a phased monitoring program to adequately characterize subsurface gas migration	23
• Use of predictive models to estimate extent of subsurface gas migration	24
AIR	
• Use of dispersion modeling and meteorological/emissions monitoring data to estimate downwind contaminant concentrations	25
• Design of an upwind/downwind monitoring program when multiple sources are involved	26
SURFACE WATER	
• Use of existing site-specific data to design a surface water monitoring program	27
• Use of bioassays and bioaccumulation studies to assess potential biological effects of off-site contaminant migration	28
• Use of sediment sampling to indicate off-site contaminant migration via surface runoff	29
• Design of a sampling program to account for three-dimensional variations in contaminant distribution	30
• Use of dispersion zone concepts in the design of a surface water monitoring program	31

15.0 CASE STUDIES

CASE STUDY 1: USE OF THE 40 CFR 261 LISTING BACKGROUND DOCUMENTS FOR SELECTING MONITORING CONSTITUENTS

Point Illustrated

- The 40 CFR 261 Listing Background Documents can be of direct help in selecting monitoring constituents.

Introduction

The RCRA Hazardous Waste Listing Background Documents developed for the identification and listing of hazardous wastes under 40 CFR Part 261 represent one source of potential information on waste-specific constituents and their physical and chemical characteristics. The documents contain information on the generation, composition, and management of listed waste streams from generic and industry-specific sources. In addition to identifying hazardous constituents that are present in the wastes, the documents may also provide data on potential decomposition products. In some background documents, migratory potentials are discussed and exposure pathways are identified.

Appendix B of the Listing Document provides more detailed information on the fate and transport of hazardous constituents. Major physical and chemical properties of selected constituents are listed, including molecular weights, vapor pressures and solubilities, octanol-water partition coefficients, hydrolysis rates, biodegradation rates, and volatilization rates. Another section of the appendix estimates the migratory potential and environmental persistence of selected constituents based on a conceptual model of disposal in an unconfined landfill or lagoon.

The appropriate uses and limitations of the Listing Documents are outlined in Table 15-1. A case study on how the Documents may be used in investigating a release follows.

TABLE 15-1

USES AND LIMITATIONS OF THE LISTING BACKGROUND DOCUMENTS

Uses	Limitations
• Identifies the hazardous constituents for which a waste was listed	• Applicable only for listed hazardous wastes
• In some cases, provides information on additional hazardous constituents which may be present in a listed waste	• Industry coverage may be limited in scope (e.g., the wood preserving industry). Listing Documents only cover organic preservatives, not inorganics (15 percent of the industry), such as inorganic arsenic salts
• In some cases, identifies decomposition products of hazardous constituents	• Data may not be comprehensive (i.e., not all potentially hazardous constituents may be identified). Generally, limited to the most toxic constituents common to the industry as a whole
• Provides overview of industry; gives perspective on range of waste generated (both quantity and general characteristics)	• Data may not be specific. Constituents and waste characteristic data often represent an industry average which encompases many different types of production processes and waste treatment operations
• May provide waste-specific characteristics data such as density, pH, and leachability	• Listing Documents were developed from data/reports available to EPA at the time, resulting in varying levels of detail for different documents
• May provide useful information on the migratory potential, mobility, and environmental persistence of certain hazardous constituents	• Hazardous waste listings are periodically updated and revised, yet this may not be reflected in the Listing Documents
• May list physical and chemical properties of selected constituents	• Listing Documents for certain industries (e.g., the pesticides industry) may be subject to CBI censorship due to the presence of confidential business information. In such cases, constituent data may be unavailable (i.e., expurgated from the document)

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Facility Description

The facility is a wood preserving plant located in the southeast. The facility uses a steaming process to treat southern pine and timber. Contaminated vapors from the wood treating process are condensed and transported to an oil/water separator to reclaim free oils and preserving chemicals. The bottom sediment sludge from this and subsequent waste water treatment units is a RCRA listed hazardous waste: K001.

Use of Listing Background Documents

Due to the presence of small, but detectable, levels of phenolic compounds in the ground water of an adjacent property, a RCRA Facility Assessment (RFA) was conducted and it was determined that a release from the facility had occurred. The owner was instructed to conduct a RCRA Facility Investigation (RFI). Before embarking on an extensive waste sampling and analysis program, the owner decided to explore existing sources of information in order to better focus analytical efforts.

The owner obtained a copy of the Wood Preserving Industry Listing Background Document from the RCRA Docket at EPA Headquarters. He also had available a copy of 40 CFR Part 261, Appendix VII, which identifies the hazardous constituents for which his waste was listed. For K001, he found the following hazardous constituents listed: pentachlorophenol, phenol, 2-chlorophenol, p-chloro-m-cresol, 2,4-dimethylphenyl, 2,4-dinitrophenol, trichlorophenols, tetrachlorophenols, 2,4-dichlorophenol, creosote, chrysene, naphthalene, fluoranthene, benz(b)fluoranthene, benz(a)pyrene, ideno(1,2,3-cd)pyrene, benz(a)anthracene, dibenz(a)anthracene, and acenaphthalene.

From the Summary of Basis for Listing section in the Listing Document, the owner found that phenolic compounds are associated with waste generated from the use of pentachlorophenol-based wood preservatives, and that polynuclear aromatic hydrocarbons (PAHs) (i.e., chrysene through acenaphthalene in Appendix VII) are associated with wastes from the use of creosote-based preservatives. Examining the facility records, he determined that pentachlorophenol had been the

sole preservative used; moreover, it had come from a single manufacturer. Based on a demonstrable absence of creosote use, the owner felt confident in excluding creosote and PAHs.

To help focus on which phenolics might be present in his waste, the owner turned to the Composition section of the Listing Document. In Table 4, he found typical compositions of commercial grade pentachlorophenol. The sample from his manufacturer contained 84.6 percent pentachlorophenol, 3 percent tetrachlorophenol, and ppm levels of polychlorinated dibenzo-p-dioxins and dibenzo-furans. The owner was surprised by the absence of the other phenolics mentioned in Appendix VII, and he was concerned by the presence of dioxins and furans. Reading the text carefully, he discovered that the majority of the phenolic compounds listed as hazardous constituents of the waste are actually decomposition products of penta- and tetrachlorophenol. He also learned that while the Agency had ruled out the presence of tetrachlorodibenzo(p)dioxin (TCDD) in the listed waste (except where incinerated), it had not ruled out the possibility that other chlorinated dioxins might be present: "... chlorinated dioxins have been found in commercial pentachlorophenol and could therefore be expected to be present in very small amounts in some wastes." Due to their extreme toxicity and because his facility had historically used the commercial pentachlorophenol with the highest concentration of dioxins and furans, the owner thought it prudent to include a scan for dioxins in his waste analysis plan.

The owner found no further data in the Composition section to help him narrow the list of phenolics; however, Table 6 gave a breakdown of organic compounds found in different wood preserving plants (i.e., steam process vs. Boneton conditioning), but only two phenolics were listed. A note in the text highlights one of the limitations of using the Listing Document: "The absence in this table (Table 6) of certain components ... probably indicates that an analysis for their presence was not performed rather than an actual absence of the component." It should be kept in mind that the waste analyses in the Listing Background Documents are not comprehensive and that they are based, as the Agency acknowledges, on data available at the time. In the absence of more detailed waste-specific data, the owner decided to include pentachlorophenol, tetrachlorophenol, unsubstituted phenol, and the six listed decomposition-product phenolic compounds in his waste analysis plan.

In reading the Listing Documents, the owner found useful information for other phases of the RFI. In the Migratory Potential Exposure Pathways section, he learned that pentachlorophenol is highly bioaccumulative, with an octanol/water partition coefficient of 102,000. Tetrachlorophenol, tri-chlorophenol, and dichlorophenol are likewise bioaccumulative, with octanol/water coefficients of 12,589, 4,169, and 1,380, respectively. He also learned that the biodegradability of pentachlorophenol is concentration limited.

In Appendix B of the Listing Background Documents; Fate and Transport of Hazardous Constituents, the owner found data sheets for six out of nine phenolic compounds, also some for dioxins and furans. Information on water chemistry, soil attenuation, environmental persistence, and bioaccumulation potential were listed along with chemical and physical properties such as solubility and density.

Case Discussion

Although the Listing Background Document did not provide the owner with enough specific data to fully characterize his waste, it did help him refine the list of monitoring constituents, alert him to the potential presence of dioxins, and gave him physical and chemical waste characteristic data which could be useful in predicting contaminant mobility.

CASE STUDY 2: ESTIMATION OF DEGRADATION POTENTIAL OF CONTAMINANTS IN SOIL

Point Illustrated

- Degradation, either chemical or biological, can be an important factor in determining the fate of a contaminant in soil, and can also be a factor in identifying constituents to monitor. The degradation rate can also be accelerated as a means of conducting interim or definitive corrective measures.

Introduction

Degradation of contaminants in the environment can occur through several mechanisms, and can be a factor in identifying monitoring constituents. Under natural conditions, these processes are often very slow, but studies have shown that chemical and biological degradation can be accelerated in the soil by modifying soil conditions. Parameters such as soil moisture content and redox condition can be altered to encourage contaminant degradation in soils.

Site Description

The site is situated in an arid region that was used during the 1970s by aerial applicators of organochlorine and organophosphate pesticides. The applicators abandoned the site in 1980 and homes were built in the vicinity. The site can be divided into three areas based on past use. The most contaminated area, the "hot zone", is a 125 feet by 50 feet area at the north end of the site that was used for mixing, loading, and unloading the pesticides. Soil samples from this area contained toxaphene, ethyl parathion, and methyl parathion at concentrations up to 15,000 mg/kg. The present residential area was used as a taxiway and an area to rinse tanks and clean planes. Soils from this zone were low in parathions but toxaphene concentrations ranging from 20 to 700 mg/kg were found. This area is approximately 1.7 acres in size and located immediately south and west of the hot zone. The runway itself was approximately 10 acres in size and south of the residential zone. Soil sample results from the runway area had low concentrations of all three pesticides.

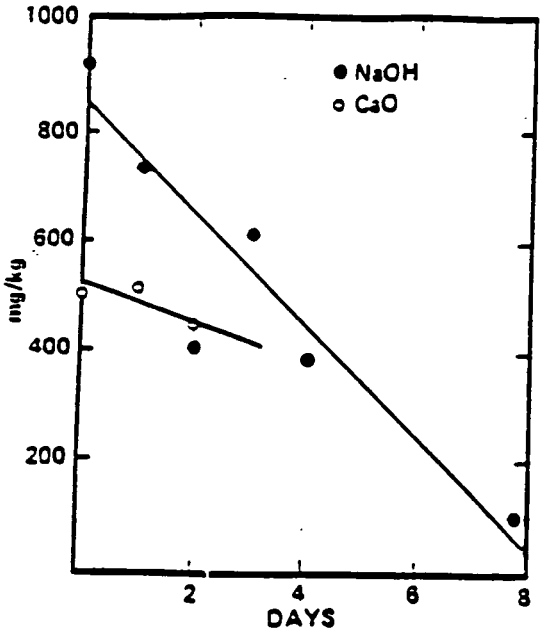
A number of factors influence degradation of organic compounds in soils. These include:

- chemical nature of the compound
- organic matter content of the soil
- soil pH
- oxidation/reduction environment of the soil
- concentrations of the compound.

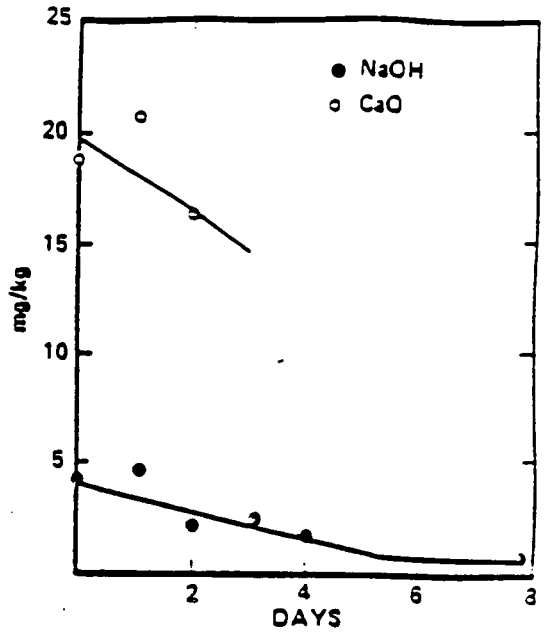
At the subject site, the soils were low in moisture content, were oxidizing, and exhibited soil pH values of 6.8 to 8.0. Under such conditions, parathion can be degraded slowly by alkali catalyzed hydrolysis reactions. The rate of these reactions increases with increasing soil pH. Parathion can also be biodegraded to O,O-Diethyl phosphoric acid. At a nearby site, it was shown that toxaphene will degrade anaerobically if reducing conditions can be achieved in the soil. It has also been observed that the loss of toxaphene by volatilization is enhanced by high soil moisture content. Other data indicated that toxaphene will degrade in the presence of strong alkali, by dechlorination reactions. This information can be used in identifying monitoring constituents and in performing interim and definitive corrective measures.

To test the feasibility of chemically degrading the contaminated soil, in situ, laboratory bench-scale tests were performed. Two treatments were evaluated, application of calcium oxide (quicklime) and sodium hydroxide (lye). Figure 15-1 shows that the pesticides were degraded by both of these strong alkalis.

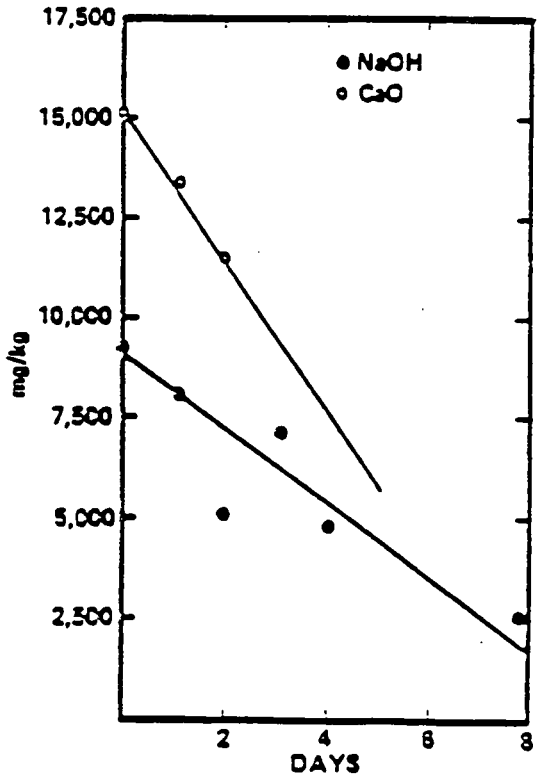
Those responsible for the remedial measures felt that the hot zone was too contaminated for in situ treatment to be effective over reasonable time periods. The upper 2 feet of soil from this area was excavated and transported to an approved landfill for disposal. However, the 1.7-acre residential area was treated in situ. To promote degradation, approximately 200 g/ft^2 of sodium hydroxide was applied using a tractor with a fertilizer-spreading attachment. A plow and disc were used to mix the sodium hydroxide into the soil to a depth of 1.5 feet. At 70 days after the application, concentrations of ethyl parathion had decreased by 76 percent, methyl parathion by 98 percent, and toxaphene by 45 percent. 390



Laboratory Bench Test, Ethyl Parathion Degradation



Laboratory Bench Test, Methyl Parathion Degradation



Laboratory Bench Test, Toxaphene Degradation

Figure 15-1. Results of Laboratory Bench Test for Pesticide Degradation

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Source: (from King et al., 1988).

Case Discussion

Knowledge of the properties of a contaminant as well as its environment are important in assessing the potential for degradation, and this information can be used to identify monitoring constituents and conduct interim or definitive corrective measures. It may be possible to alter the site's physical or chemical characterisitcs to enhance degradation of contaminants. Under appropriate conditions, in situ treatment of contaminated soils can be an effective corrective measures method.

Reference

King, J., T. Tinto, and M. Ridosh. 1985. In Situ Treatment of Pesticide Contaminated Soils. Proceedings of the National Conference of Management of Uncontrolled Hazardous Waste Sites. Washington, D.C.

CASE STUDY 3: SELECTION AND EVALUATION OF A SOIL SAMPLING SCHEME

Points Illustrated

- Sampling methodologies must be properly selected to most appropriately characterize soil contamination.
- Statistical analyses can be used to evaluate the effectiveness of a chosen sampling scheme.

Introduction

Selection of a sampling scheme appropriate for a soil contamination problem is dependent on the objectives of the sampling program. A grab sampling scheme may be employed; however, grab sampling can produce a biased representation of contaminant concentrations because areas of gross contamination are most often chosen for sampling. Random sampling can provide an estimate of average contaminant concentrations across a site, but does not take into account differences due to the proximity to waste sources and soil or subsurface heterogeneities. A stratified random sampling scheme allows these factors to be considered and, thus, can be appropriate for sampling. Depending on the site, additional sampling using a grid system may be needed to further define the areas of contamination.

Facility Description

The example facility operated as a secondary lead smelter from World War II until 1984. Principal operations at the smelter involved recovery of lead from scrap batteries. Air emissions were not controlled until 1968, resulting in gross contamination of local soils by lead particulates.

Land use around the smelter is primarily residential mixed with commercial/industrial. A major housing development is located to the northeast and a 400-acre complex of single family homes is located to the northwest. Elevated blood lead levels have been documented in children living in the area.

Program Design/Data Collection

Initial soil sampling was conducted at the lead smelter and in the surrounding area to document suspected contamination. Sample locations were selected based on suspected areas of deposition of airborne lead and in areas where waste dumping was known to have occurred. High lead concentrations were documented in samples collected from these sources. Because data obtained in the exploratory sampling program (grab sampling) were not adequate to delineate the areal extent of contamination, a stratified random sampling scheme was developed.

Based on wind rose data and the behavior of airborne particulate matter, a sampling area was selected encompassing a 2-mile radius from the smelter. Specific sampling sites were selected using a stratified random sampling scheme. The study area was divided into sectors each 22.5 degrees wide and aligned so that prevailing winds bisected the sectors. Each sector was further divided into approximately one-tenth mile sections. A random number generator was used to select first the direction and then the section. Random numbers generated were subject to the following restrictions: two-thirds of the sites selected had to fall in the major downwind direction; both residential and non-residential sites had to exist in the sector; sampling sections were eligible for repeat selection only if they were geographically within 1/2 mile of the smelter or if the section contained both residential and non-residential sites. Sites that were biased towards lead contamination from other than the lead smelter were not sampled (e.g., gas stations and next to roads). A total of 20 soil sampling locations were selected, 10 at residences and 10 at non-residential sites such as schools, parks, playgrounds and daycare centers.

Sample cores were collected using a 3/4-inch inner diameter stainless steel corer. Total sample depth was 3 inches. A minimum of four and maximum of six samples were collected at each sampling location within a 2 ft radius. Cores were divided into 1 inch increments and the corresponding increments were composited from each depth to make up one sample. This approach provided data on lead stratification in the top 3 inches of soil. All samples were analyzed for total lead.

The results of the stratified random sampling indicated several acres with over 2,000 ppm lead in the soil. To further define the extent of these areas, a grid sampling plan was designed. Seven hundred and fifty foot increments were used. The grid was oriented along the axis of the release. Both residential and non-residential areas were sampled. At each grid point, four 3-inch cores were collected 30 m from the grid point in each major compass direction. The cores were composited by depth as discussed above.

Program Results/Data Anaysis

Analytical results from the soil sampling program indicated significant lead contamination within the study area. Maximum concentrations observed were 2,000 ppm lead with a background level of 300 ppm. Krieging of the data from the grid sampling plan was used to develop a contour map as shown in Figure 15-2. Lead concentrations were highest northwest and southwest of the smelter.

Case Discussion

Because of the large area potentially affected by lead emissions, development of a sequential sampling plan was necessary to determine the maximum soil lead concentrations surrounding the smelter and the areas having elevated concentrations. A grab sampling scheme was first used to confirm that soil contamination existed. A stratified random sampling scheme was developed to provide representative data throughout the study area. This type of sampling allowed consideration of prevailing wind directions and the need to sample both residential and non-residential areas. To further define areas of contamination, a grid sampling plan was developed. From these data, lead isoconcentrations maps were prepared delineating areas with elevated concentrations.

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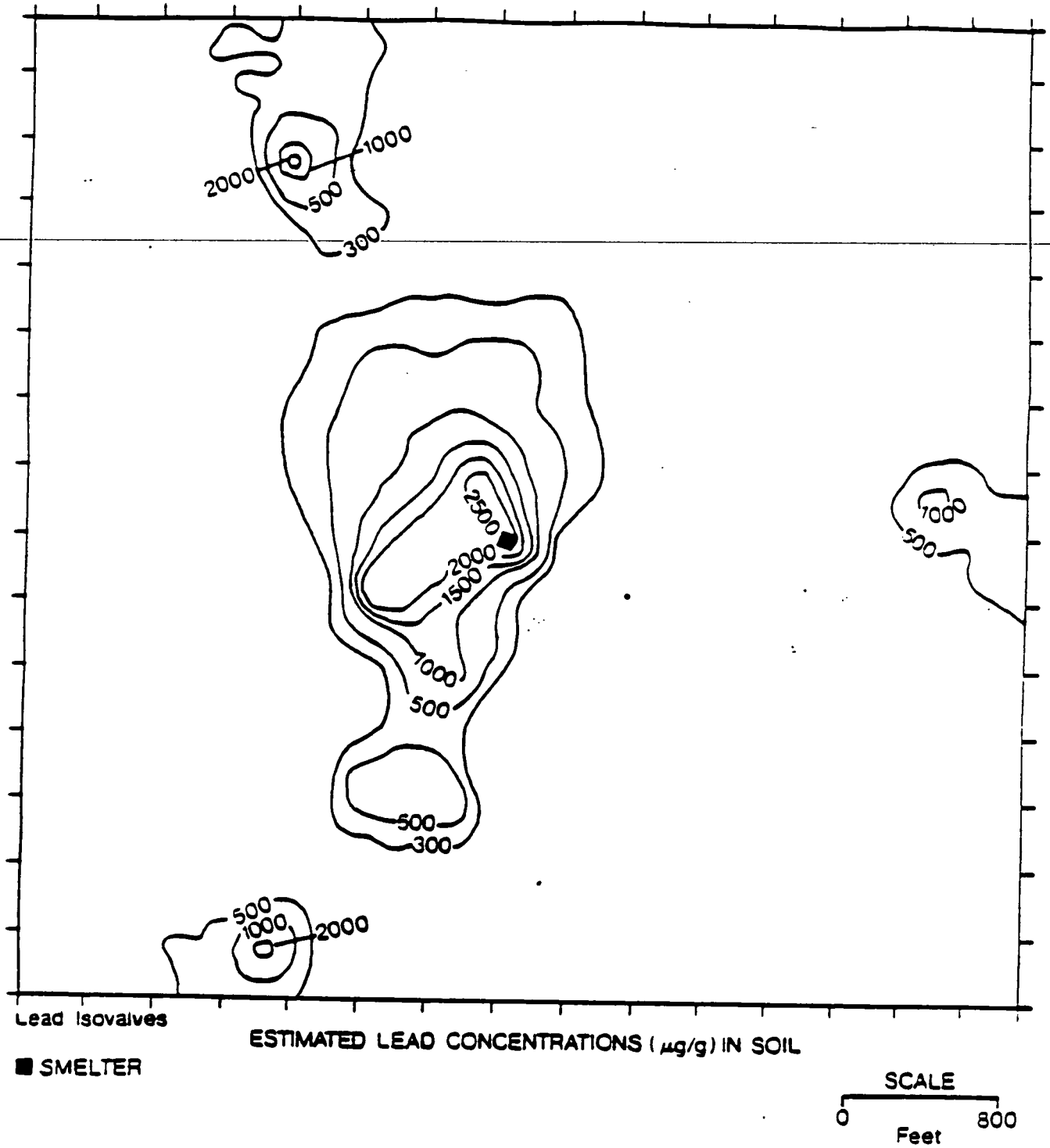

Figure 15-2. Isoconcentration Map of the Lead Concentrations in ppm Around the Smelter

CASE STUDY 4: SAMPLING OF LEACHATE FROM A DRUM DISPOSAL AREA WHEN EXCAVATION AND SAMPLING OF DRUMS IS NOT PRACTICAL

Points Illustrated

- It is not always possible to perform waste characterization prior to establishing the RFI monitoring scheme because the waste may not be directly accessible, as in the case of buried drums.

- When direct waste characterization is not practical, release monitoring should be performed for the constituents listed in Appendix B of Volume I of the RFI Guidance.

Introduction

Insufficient waste characterization data existed for a former drum disposal facility that was suspected of releasing contaminants into the subsurface environment. Leachate within the disposal pit was sampled and analyzed for all constituents listed in Appendix B of Volume I of the RFI Guidance. The resulting information was used to determine the major waste constituents to be monitored during the RFI.

Facility Description

The unit of concern was a pit containing an estimated 15,000 drums. Due to poor recordkeeping by the facility operator, adequate information regarding the contents of the drums was not available. It was also not known if the drums were leaking and releasing contaminants to the environment. Because insufficient data existed regarding the drum contents, it was not known what constituents should be monitored in nearby ground and surface waters. Due to the risk to workers and the potential for causing a multi-media environmental release, excavation and sampling of the drums to determine their contents was not considered practical. Instead, it was decided that leachate around the perimeter of the drum disposal pit would be sampled to identify constituents which may be of concern.

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Program Design/Data Collection

To determine the physical extent of the buried drums, a geophysical survey was conducted using a magnetometer. Borings were located at positions having lower magnetometer readings than surrounding areas in order to minimize the potential for drilling into drums.

Soil borings were drilled around the perimeter of the drum disposal pit, as defined by the magnetometer survey. Drilling was accomplished using a hydraulic rotary drill rig with a continuous cavity pump. Water was used as the drilling fluid. To prevent surface runoff from entering the borehole and to control gaseous releases from the borehole, primary and secondary surface collars were installed. These consisted of 5-foot sections of 4-inch steel pipe set in concrete. A device to control liquid and gaseous releases from the borehole was threaded onto the collars to form a closed system (Figure 15-3).

Drilling was performed using a wireline operated tri-cone roller bit with a diamond tipped casing advancer (Figure 15-4). Water was pumped down inside the casing and out the drill bit, returning up the borehole or entering the formation. The use of water to aid in drilling also helped reduce the escape of gases from the borehole. Air monitoring showed no releases. Split-spoon samples were collected at 5-foot intervals during the drilling and a leachate monitoring well was installed at each boring location.

The soil and leachate samples were analyzed for the compounds contained in Appendix B of Volume I of the RFI Guidance.

Program Results/Data Analysis

The leachate samples were found to contain high levels of volatile organic compounds including 2-butanone, 4-methyl-2-pentanone, and toluene. Concentrations were higher on the downgradient side of the pit.

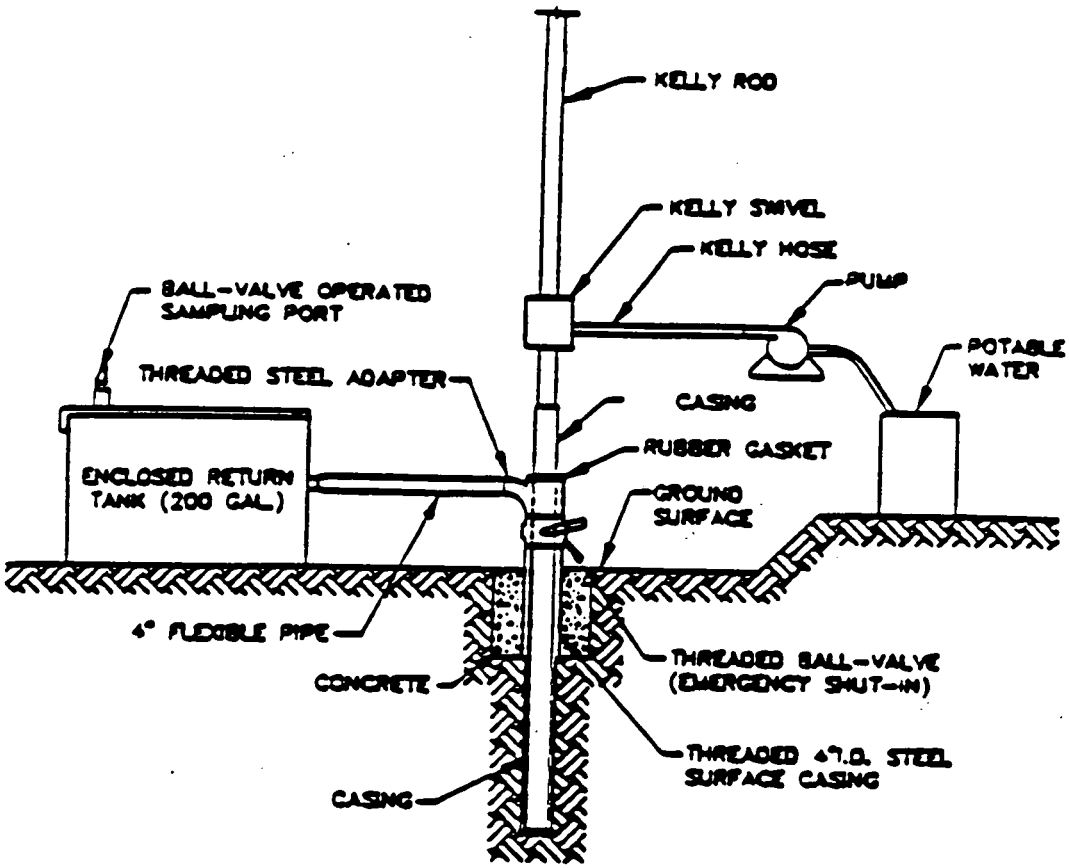

Figure 15-3. Schematic Diagram of Gas Control System Utilized at Pit

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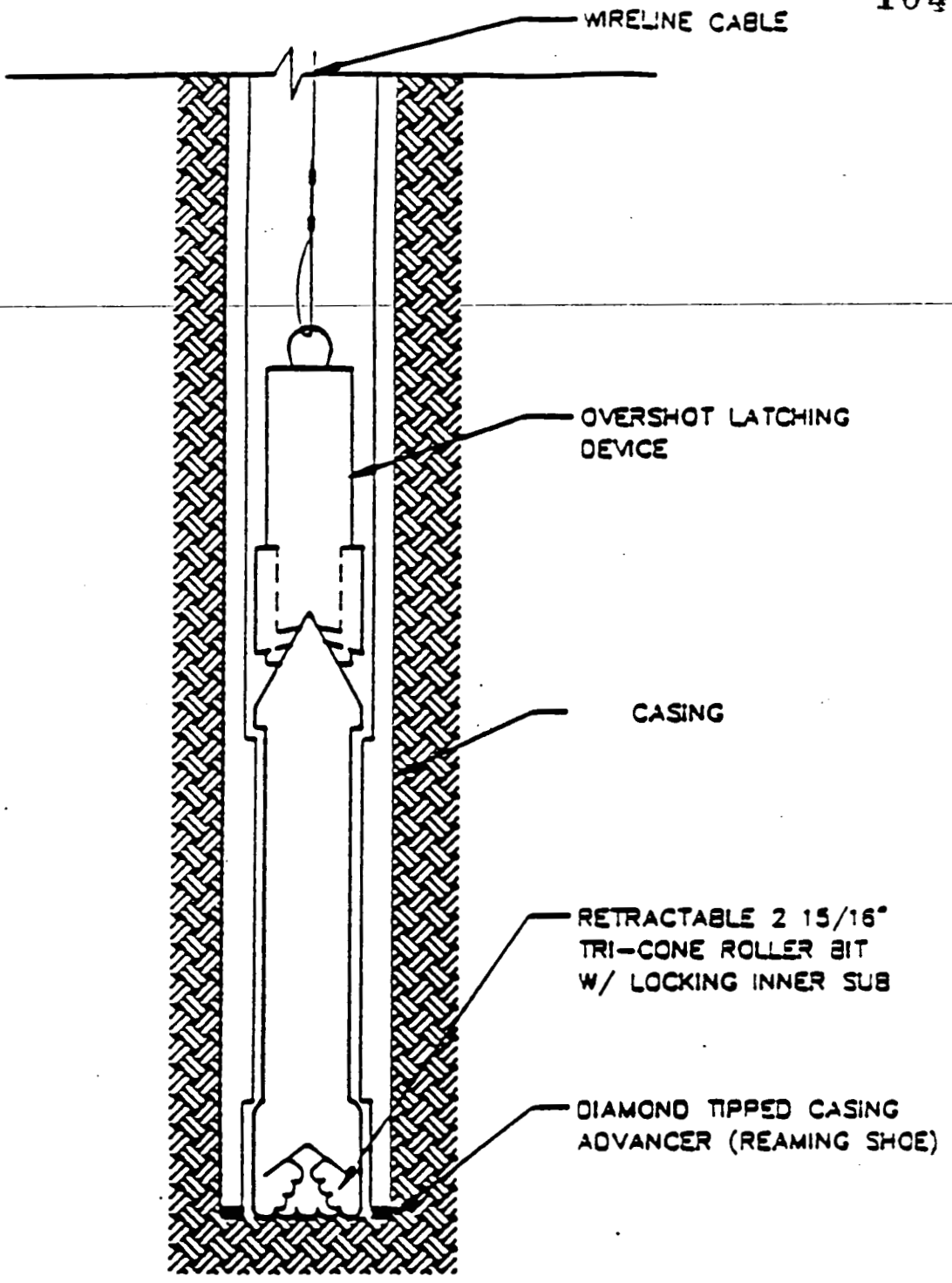

Figure 15-4. Schematic Drawing of Wireline Drill Bit and Reaming Shoe

Case Discussion

Leachate sampling can be useful in determining whether buried drums are leaking and to identify materials that are being released. This methodology can be safer than excavation and sampling of individual drums. It can also identify the more soil-mobile constituents of the leachate.

The data gathered in this case study were used in designing a monitoring program, and the contaminants found were used as indicator compounds to link downgradient ground-water contamination to this waste disposal unit.

CASE STUDY 5: USE OF QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) AND DATA VALIDATION PROCEDURES

Points Illustrated

- A comprehensive field and laboratory QA/QC program is necessary for assessing the quality of data collected during an RFI.
- Timely validation of laboratory data can uncover problems correctable by reanalysis or by resampling, thus preventing data gaps.

Introduction

A company in the mining and smelting industry sampled domestic wells and surface soils in the vicinity of a tailings pile to monitor possible leaching of metals into the aquifer and possible soil contamination due to wind-blown dust. Because the data would be used to assess corrective measures alternatives and to conduct a health and environmental assessment, the company chose to conduct both its sampling and analysis efforts under a formal QA/QC Project Plan and to subject all laboratory data to rigorous data validation procedures.

Facility Description

At this facility, a tailings pond had received smelter waste for many years. Local water supply wells were potentially at risk due to percolation of water through the pile and possible leaching of heavy metals. Local surface soils in nearby residential areas (e.g., yards, public playgrounds) were also subject to contamination from wind-blown dust originating from the pile during dry windy weather.

Sampling Program

Before sampling began, a set of documents were drafted following U.S. EPA guidelines (U.S. EPA 1978, 1980a, 1980b, 1981, 1982, 1985a, 1985b) that specified in detail sampling sites and parameters to be measured, field and laboratory

procedures, analytical laboratory protocols, and all field and laboratory QC checks including frequencies, and corrective actions. The important elements of each document are described below.

Standard Operating Procedures (SOPs)--

This document contained step-by-step procedures for the following items:

- Calibration, operation, and maintenance of all instruments used in the field and laboratory.
- Equipment decontamination.
- Ground water and soil sampling, including compositing.
- Use of field notebooks and document control.
- Sample packaging, shipping, and chain-of-custody.

Field Operations Plan (FOP)--

This document included the following:

- Rationale for choice of sampling locations, sampling frequency, and analytes to be measured
- List of sampling equipment and SOPs to be used for each sampling event.
- List of field QC checks to be used and their frequency for each sampling event.
- Health and safety issues and protective measures for field personnel.
- Sampling schedule.

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Laboratory Analytical Protocol (LAP)--

This document included the following:

- Sample size, preservation, and analysis protocol for each analyte.
- List of laboratory QC checks, QC statistics to be calculated and their control limits, and corrective actions for QC checks outside control limits.
- Detailed list of deliverable documents and their formats.
- Procedures for sample custody, independent audits, and general laboratory practices.

QA/QC Project Plan (QAPP)--

This document gathered into one place the overall data quality objectives for the sampling and detailed QC procedures needed to attain those objectives. Included were:

- Quality assurance objectives in terms of precision, accuracy, completeness, comparability, and representativeness.
- Procedures for the screening of existing data.
- Data management, reduction, validation, and reporting.
- Overview of both field and laboratory QC checks and their frequencies, control limits, and corrective actions.
- Data assessment procedures.

Results

Five surface soil samples were taken in high traffic areas of two playgrounds and three residential yards. Five tap water samples were collected at two public

drinking fountains at the playgrounds and at the three private residences. The analysis results, as received from the laboratory, are shown in Table 15-2. The data indicated that a soil hot spot existed for cadmium, that elevated lead occurred at all five soil stations, and that all of the domestic wells showed elevated levels of mercury.

The laboratory data package was subjected to a thorough data validation, as detailed in the QA Project Plan. The following information and QC results were checked by examination of original documents or photocopies of the documents.

Sampling, Sample Shipping, Chain-of-Custody--

Copies of field and field laboratory notebook pages were examined to insure that all SOPs were correctly followed, that there were no notations of anomalous circumstances (such as sample spillage) that may have affected analysis results, and that the samples were correctly preserved, packaged, and shipped. Copies of all chain-of-custody forms, bills-of-lading, and sample analysis request forms were examined to insure that chain-of-custody was not broken and that samples arrived intact at the laboratory.

Laboratory Raw Data--

The QAPP had specified that one of the deliverables from the laboratory was copies of all instrument readouts and laboratory notebook pages. The digestion raw data were checked to insure that no holding time violations had occurred. This is important for mercury because the holding time is only 28 days for aqueous samples.

All raw calibration data were recalculated and tested against instrument-calculated sample results. Recoveries of calibration verification standards and continuing calibration standards were checked to insure that all instruments were correctly calibrated, were not drifting out of calibration, and were correctly calculating raw analysis results.

TABLE 15-2

RESULTS OF ORIGINAL SURFACE SOIL AND TAP WATER ANALYSES

Sample[a]	Cd	Cu	Pb	Hg	Zn
SOIL-1	14	5200	800	NA[b]	1200
SOIL-2	7	2400	400	NA	190
SOIL-3	<20[c]	720	4530	NA	70
SOIL-4	19	680	350	NA	350
SOIL-5	1200	1080	460	NA	420
WATER-1	<50	NA	<30	1.5	NA
WATER-2	<50	NA	<30	1.3	NA
WATER 3	<50	NA	<30	1.0	NA
WATER-4	<50	NA	<30	1.4	NA
WATER-5	<50	NA	<30	1.2	NA

a Soils in units of mg/kg, water in µg/L.
b Not analyzed.
c Undetected at detection limit shown.

Final analysis results were recalculated from raw data using dilution and digestion factors, as summarized in the lab notebooks, and compared to the data summary sheets. No transcription errors were found. However, the cadmium result for SOIL-5 contained a calculation error, and the correct final result was 12 mg/kg instead of the 1200 mg/kg reported.

Laboratory QC Checks--

The QAPP had specified that the laboratory had to analyze pre-digestion duplicates and spikes, U.S. EPA laboratory control samples, and reagent blanks. The laboratory QC results are summarized in Table 15-3 and indicated accuracy and precision well within U.S. EPA guidelines. The mercury preparation blank also indicated that the tap water results were not due to laboratory digestion reagents or procedures.

Field QC Checks--

As specified in the QAPP and FOP, the following field QC samples were included with each of the soils and tap water samplings: bottle blank, field blank, standard reference material (SRM), triplicate, and an interlaboratory split to a "reference" lab. The results are summarized in Table 15-4.

Although no U.S. EPA control limits or corrective actions exist for field-generated QC checks, the results of their analysis can aid in the overall assessment of data quality. The triplicate, SRM, and interlaboratory split analyses indicated good overall analysis and sampling precision and accuracy. The field blanks indicated the possibility of mercury contamination from one of the four possible sources: the pre-cleaned bottles, the preservation reagent, the distilled water used in the field, or an external contamination source such as dust. The high positive mercury result in the water bottle blank eliminated all of these sources except the first because the bottle blanks remained sealed throughout the sampling effort.

The laboratory was immediately called and, upon personal inspection, the laboratory manager discussed the remnants of a broken thermometer bulb in the plastic tub used to acid-soak the bottles. An unused bottle from the same lot and

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TABLE 15-3

LABORATORY QC RESULTS

Analyte	Duplicate RPD[a] (%)		Spike Recovery[b] (%)		LCS[c] (%)	Soil Preparation Blank[d]	Water Preparation Blank[e]
	SOIL-2	WATER-4	SOIL-2	WATER-4			
Cd	18	NC[f]	100	98	101	<50[g]	<50
Cu	5	NA[h]	93	NA	97	<100	NA
Pb	14	NC	110	92	106	<200	<30
Hg	NA	NC	NA	103	NA	NA	<0.20
Zn	7	NA	85	NA	99	<150	NA

a RPD = relative percent difference = (difference/mean) x100. Control limits = ±35% for solids and ±20% for aqueous samples.

b Spike Recovery = $\frac{\text{(spike + sample result) - (sample result)}}{\text{(spike added)}}$ x100. Control limit = 75-125%.

c LCS = laboratory control sample. Control limit - 90-110%.

d mg/kg.

e µg/l.

f NC = not calculated due to one or both concentrations below detection limit.

g Undetected at detection limit shown.

h NA = not analyzed.

TABLE 15-4

FIELD QC RESULTS

Analyte	Triplicate CV[a] (%)		SRM Recovery[b] (%)		Interlab. RPD[e] (%)		Field Blanks[f]		Bottle Blanks[g]	
	SOIL-1	WATER-1	BCSS-1[c]	U.S. EPA[d]	SOIL-1	WATER-1	SOIL-1	WATER-1	SOIL-1	WATER-1
Cd	22	NC[h]	83	105	-12	NC	<50[i]	<50	<0.5	<0.5
Cu	3	NA[j]	94	NA	0	NA	<100	NA	<1	NA
Pb	7	NC	97	101	14	NC	<200	<200	<0.5	<0.5
Hg	NA	18	NA	103	NA	19	NA	1.1	NA	0.8
Zn	1	NA	110	NA	24	NA	<150	NA	<1	NA

a CV = coefficient of variation = (mean/standard deviation) X100.
b Recovery = (certified value/result) X100.
c National Research Council of Canada marine sediment.
d U.S. EPA Trace Metals I, Concentration #1.
e RPD = relative percent difference = [(analytical lab result - ref. lab. result)/mean] X100.
f Distilled water. Units = µg/L.
g Empty containers rinsed with digestion reagents at lab. Units = total µg.
h NC = not calculated due to at least one sample result below detection limits.
i Undetected at detection limit shown.
j NA = not analyzed.

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still at the laboratory as well as two bottles washed in previous lots were analyzed. The bottles previously washed contained no detectable mercury, and the bottle from the same lot as used in the sampling effort contained 0.75 µg. The water mercury data were rejected, and a second sampling effort using new bottles was conducted. All of the new samples contained no detectable mercury.

Discussion

This case study demonstrates the need for the establishment of a formal QA/QC program that not only specifies field QC protocols but also incorporates thorough data package validation. In this instance, a potential hot spot was found to be due to a calculation error, and potential mercury contamination of domestic well water was found to be a result of using contaminated sample containers. In the latter case, timely QA/QC review allowed for a speedy resampling effort which could be done at this site. In situations where resampling is not possible, adequate QA is crucial.

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CASE STUDY 6: PRESENTATION OF DATA COLLECTED DURING FACILITY INVESTIGATIONS

Point Illustrated

- Techniques for presentation of data for facility investigations involving multimedia contamination.

Introduction

Data acquisition and interpretation are integral parts of facility investigations. Depending on the size, complexity, and hazards posed at a particular site, significant quantities of meteorologic, hydrologic, and chemical data can be collected. To make the best use of these data, they should be presented in an easily understood and meaningful fashion. This case study focuses on widely used and easily implemented graphical techniques for data presentation.

Site Description

The site is a former copper smelter that ceased operation in the early 1980s. During the operation of the smelter, large quantities of mine tailings were slurried to tailings ponds that remain today (Figure 15-5). The tailings contain high solid phase concentrations of inorganic contaminants such as copper, zinc, lead, cadmium, and arsenic. In the Smelter Hill area, flue dust and stack emission deposition have contaminated surficial soils. Numerous other units were operated at the complex including an experimental plant designed to leach copper using ammonia. The copper leach plant is shown in Figure 15-6. Three disposal ponds (I, II, and III) received wastes slurried from the plant.

As a result of smelting and waste disposal practices, multimedia contamination of ground water, surface water, and soils has occurred. Also, episodes of air contamination have been documented due to entrainment of tailings during windy periods.

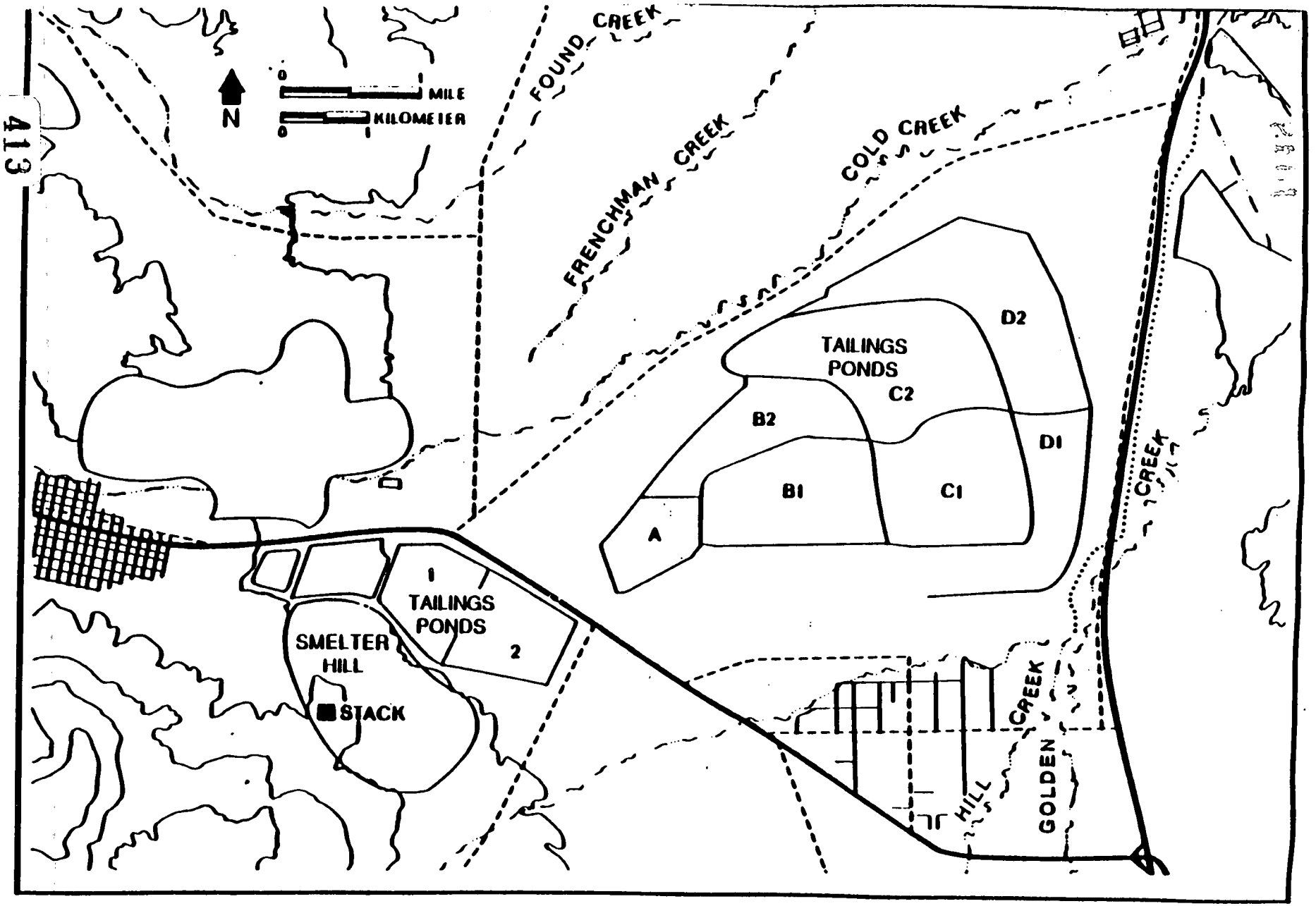

Figure 15-5. Map of the Smelter Site and Associated T onds

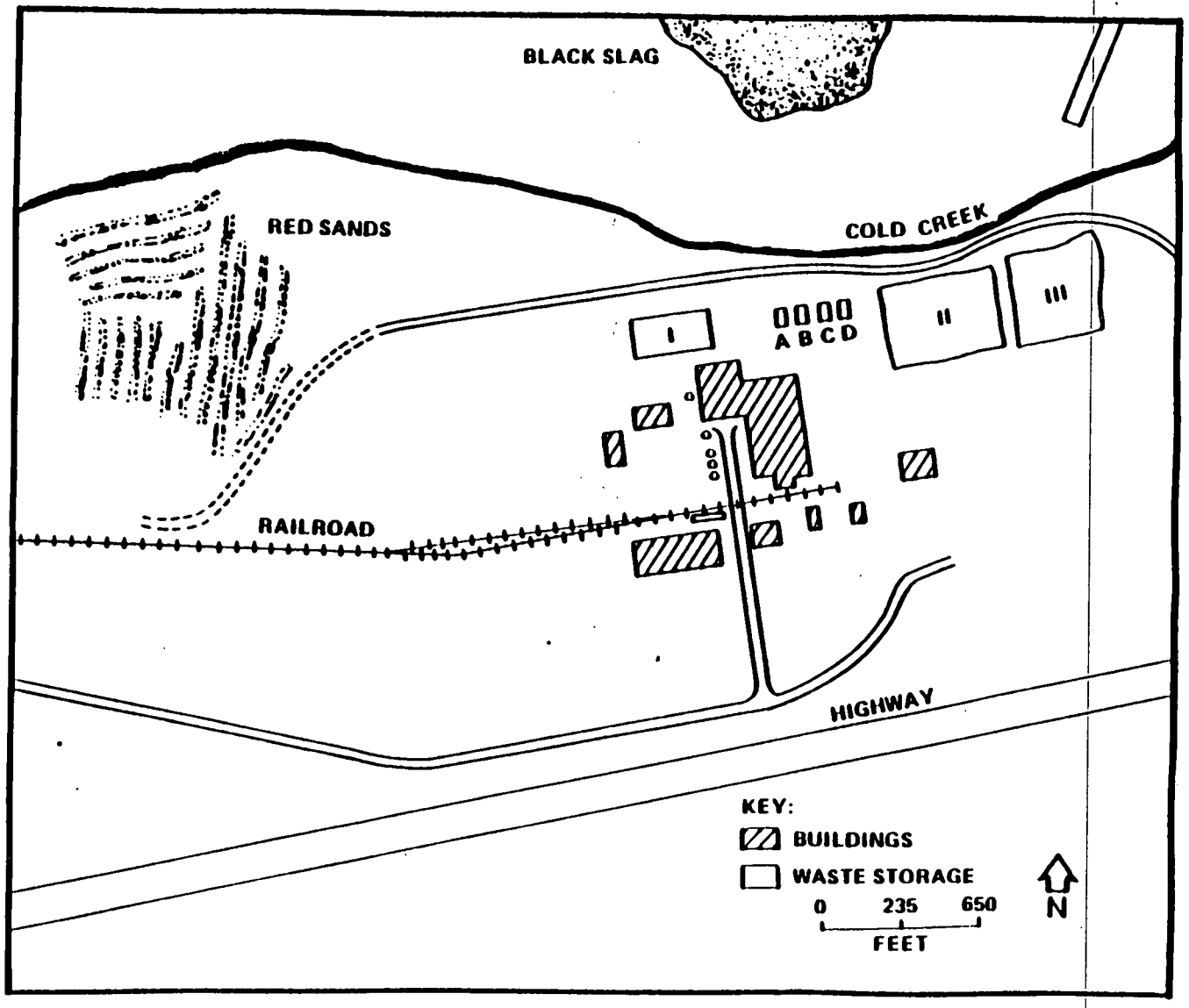

Figure 15-6. Locations of Copper Leach Plant and Waste Storage Ponds

Field Sampling and Data Collection

Data collection activities at this site were comprehensive. Over 100,000 pieces of data were collected in the categories shown in Table 15-5.

Data Presentation

This section illustrates a number of graphical techniques that can be used to present data from facility investigations. Graphical presentations are useful for the following general purposes:

- Site feature identification, source identification, and mapping;
- Hydrologic characterization; and
- Water quality characterization.

For large sites, aerial photography is often very useful for defining the locations and boundaries of waste deposits, and for establishing time variability of site characteristics. Figure 15-6, for example, was developed from aerial photographs at a 1:7800 scale. Types of information obtained by comparing this photograph to one taken 10 years earlier include:

- Pond III was originally constructed earlier than Ponds I and II, and was not lined. Ponds I and II were lined.
- The red sands (a slag deposit) shown in Figure 15-6 are present only north of the railroad tracks. Earlier photographs showed that the red sands extended to the highway, but were leveled and covered with alluvium during construction of the copper leach plant.

This type of photographic information is valuable for locating waste deposits, estimating quantities of wastes, and determining waste proximity to sensitive areas.

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TABLE 15-5

SUMMARY OF DATA COLLECTED

Category	Parameters
Ground Water	Water level elevations, potentiometric heads
	Concentration of Al, Sb, As, Ba, Be, Bo, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Mo, Ni, K, Se, Ag, Na, Sn, V, Zn, P, Cl, F, SO_4, pH, O_2, Ec, Eh, Alkalinity, TDS
Surface Water and Sediment	Flow rates, bed particle size distributions, suspended solids concentrations, dissolved concentrations of same inorganic parameters as ground water
Alluvium[a]	Moisture content, soil, pH, Ec, Sb, As, Cd, Cu, Fe, Pb, Mn, Se, Ag, Zn, particle-size distribution
Soil[a]	Cd, Cu, Fe, Pb, Mn, Ni, Zn, Sb, As, Cd, Cr, Hg, Se, Ag, Zn, particle-size distribution, Eh, S, TOC
Tailings[a]	Sb, Ar, Be, Cd, Cu, Fe, Pb, Mn, Ag, Se, Zn, particle size, moisture, pH, Ec, sulfur, carbonate
Slag and Flue Dust[a]	Sb, As, Cd, Cu, Fe, Pb, Mn, Se, Ag, Zn, SO_4, Ec, pH, alkalinity
Miscellaneous	Meteorology, aerial photographs and other photographic documentation, well log data, surface topography, volumetric surveys of waste piles

a Element data are solid phase.

For sites with complex hydrologic interaction, it is often helpful to graphically represent the flow system. Figure 15-7 illustrates the surface water system at the site. The diagram is useful because it shows the hydrologic interconnections of the drainage system.

For the ground-water system, flow direction and velocities provide information needed for contaminant transport predictions. This information is generated by plotting water levels on a site map, and then drawing contours through points of equal elevation. An example is shown in Figure 15-8. Because the contours form a relatively simple pattern in this case, they were drawn by hand. However, computer-based contour packages exist that could be used to plot more complicated contour patterns.

Inferred flow directions are also shown in Figure 15-8. From a knowledge of the hydraulic gradient, hydraulic conductivity and effective porosity, the average linear velocity can be calculated, as shown in the upper left hand corner of the figure. A velocity of 79 m/yr is calculated, for example, which means that approximately 126 years would be required for conservative solutes to move across the site (approximately 10,000 meters).

Water quality data can be presented as shown in Figure 15-9. This figure shows the spatial distribution of calcium, sulfate, and TDS at key surface water stations. This data presentation method provides a broad areal view of these parameters.

Time series plots are useful for showing temporal variations in water quality. For example, time trends of SO_4 at three ground-water monitoring locations are shown in Figure 15-10. Well 19 is slightly downgradient from the source, and the high SO_4 levels reflect that the well is receiving solutes generated within the source. Wells 26 and 24 are further upgradient, and reflect better water quality conditions. The plot indicates that variability between stations generally is more significant than time variability at a given location. One exception is at well 24 where a temporary increase in sulfate levels was noted in 1975-76.

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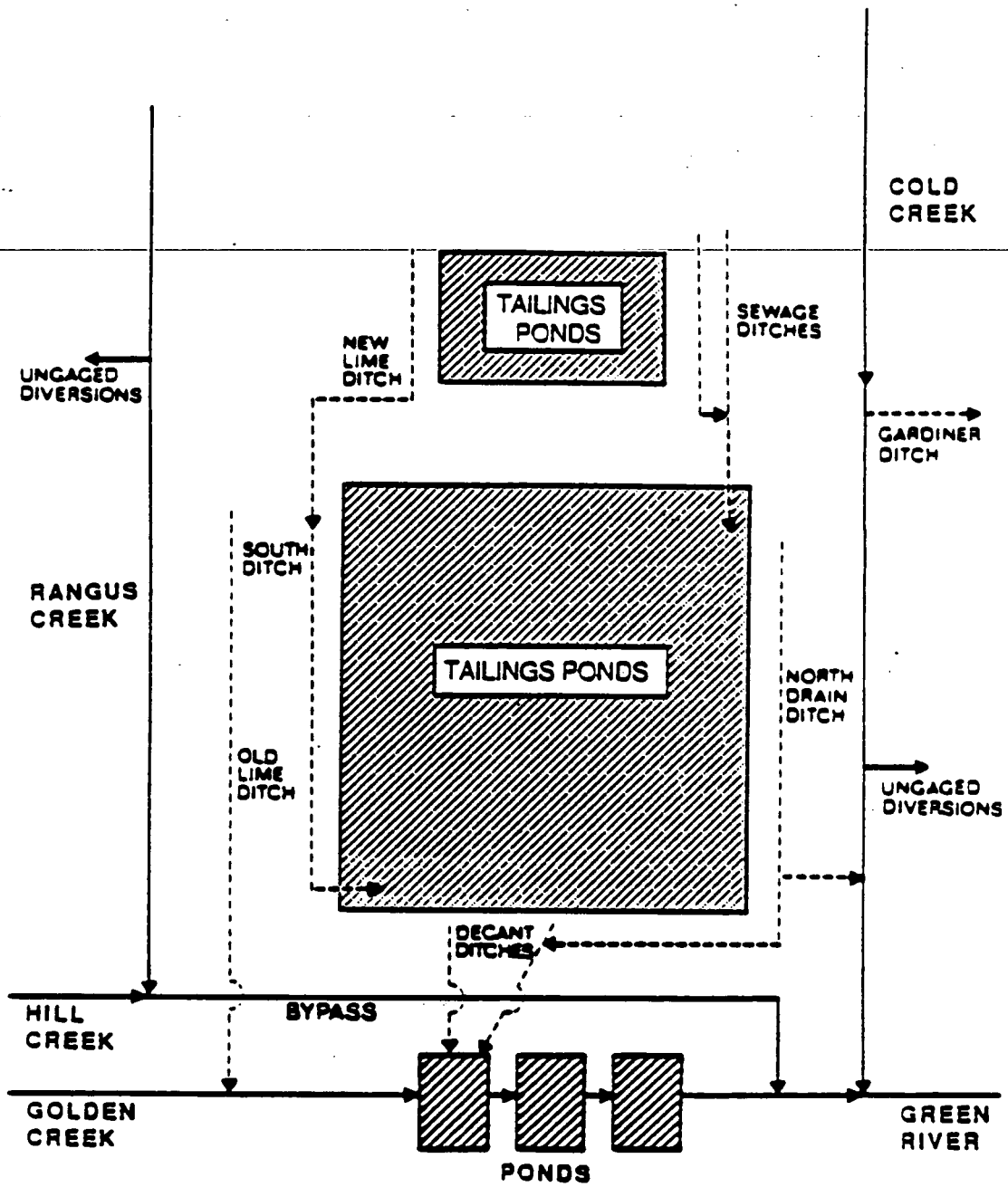


Figure 15-7. Schematic of Surface Water System

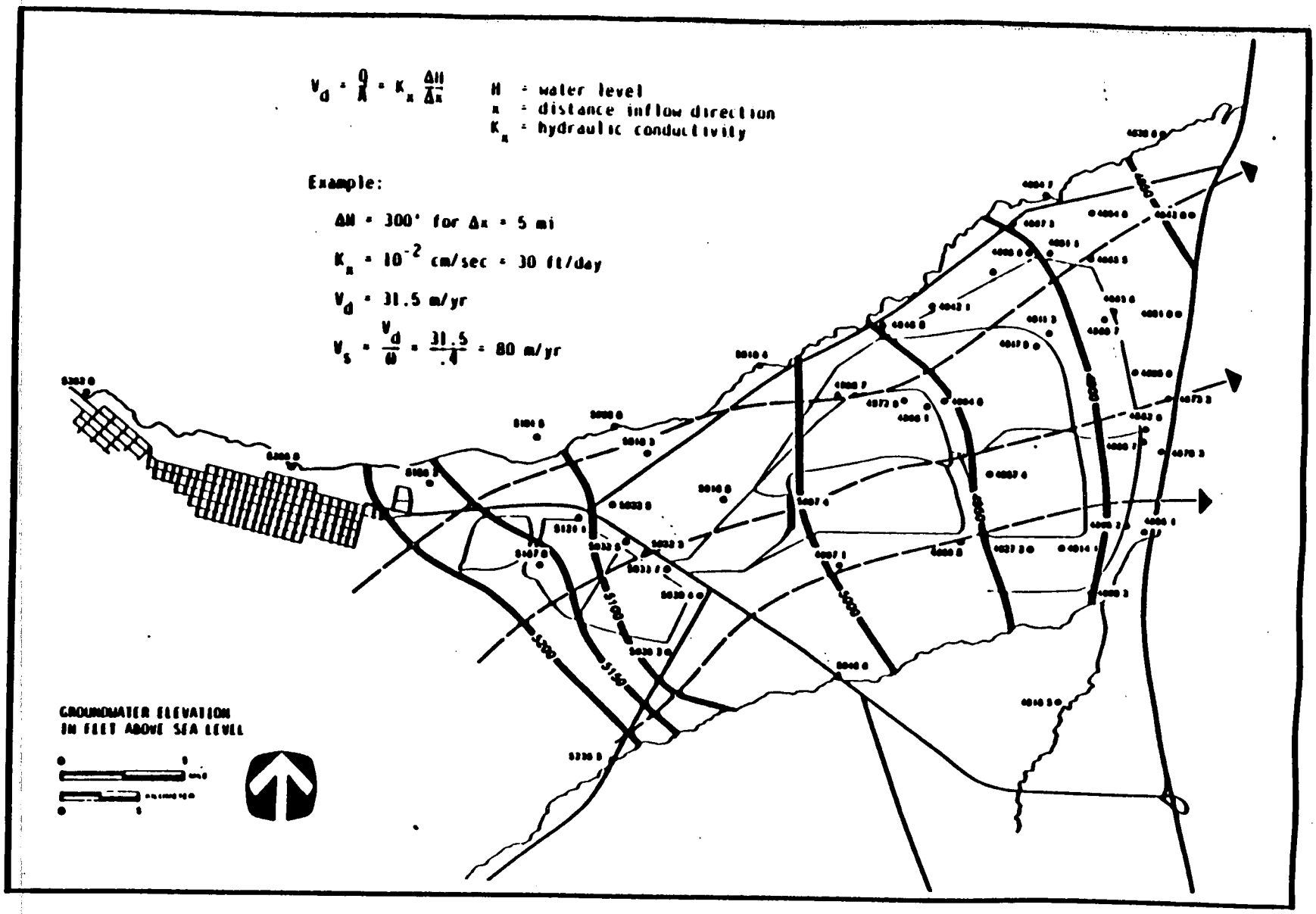


Figure 15-8. Ground-Water Flowlines Based on Measured Water Levels

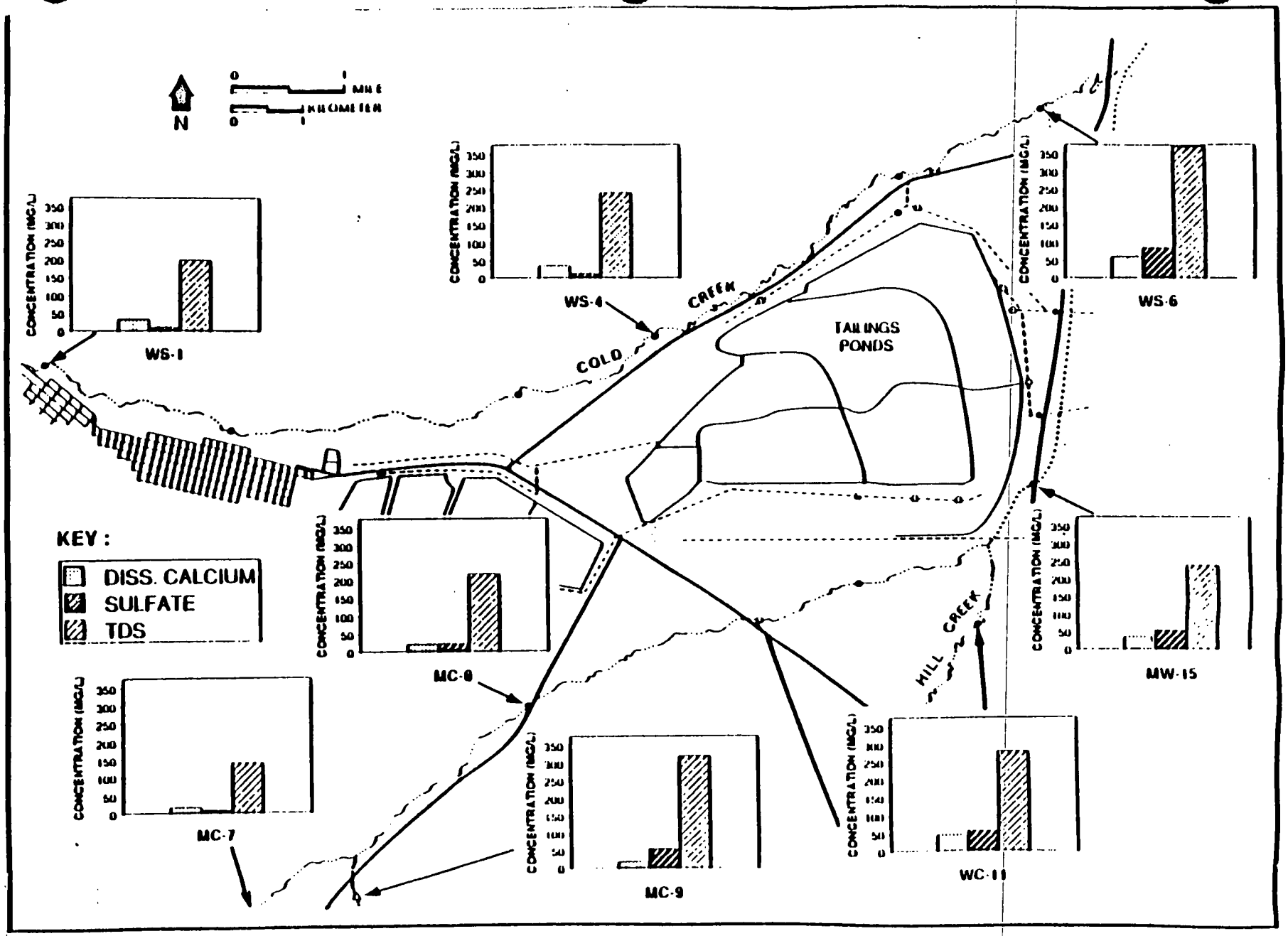


Figure 15-9. Selected Surface Water Quality Parameters at Key Stations

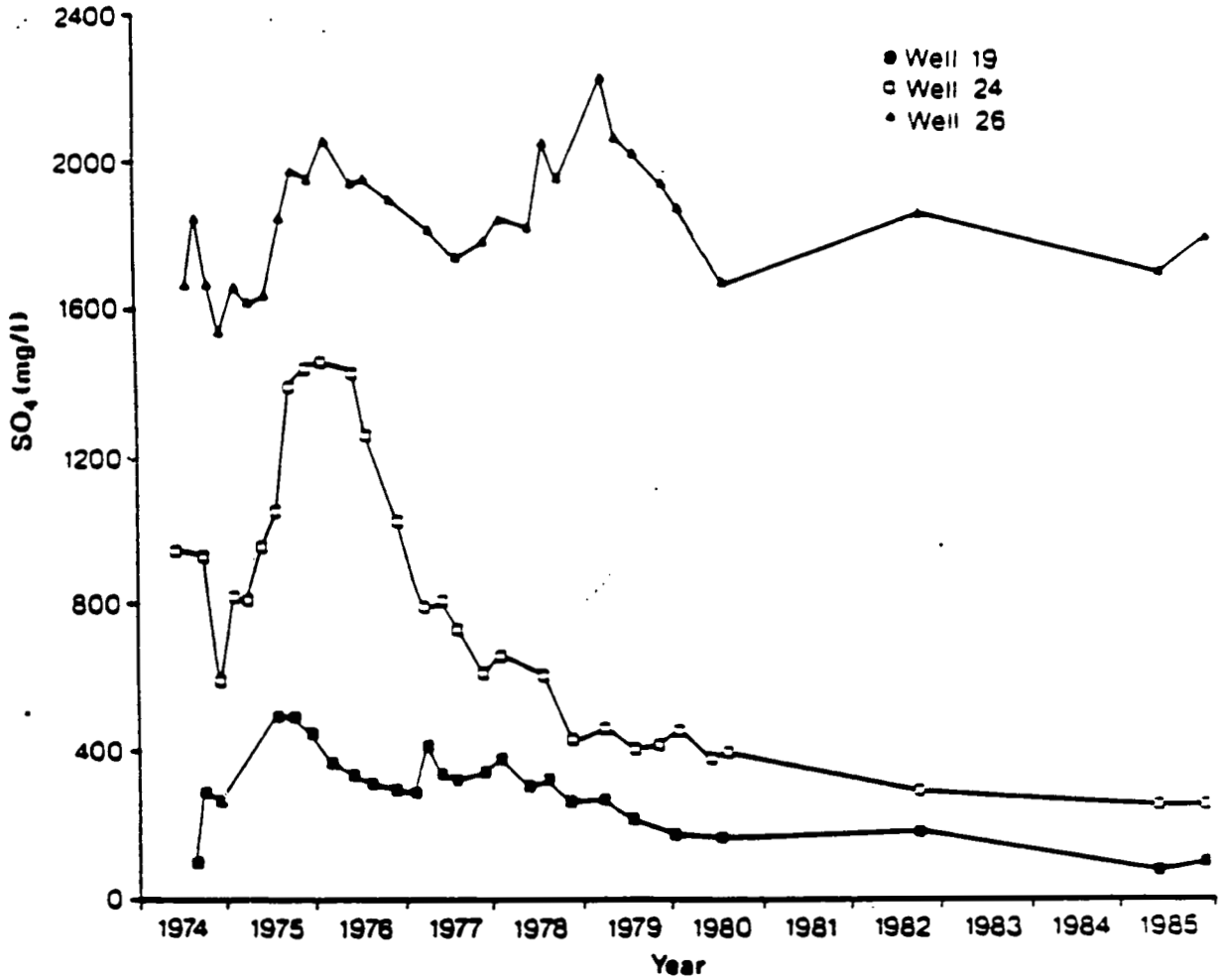


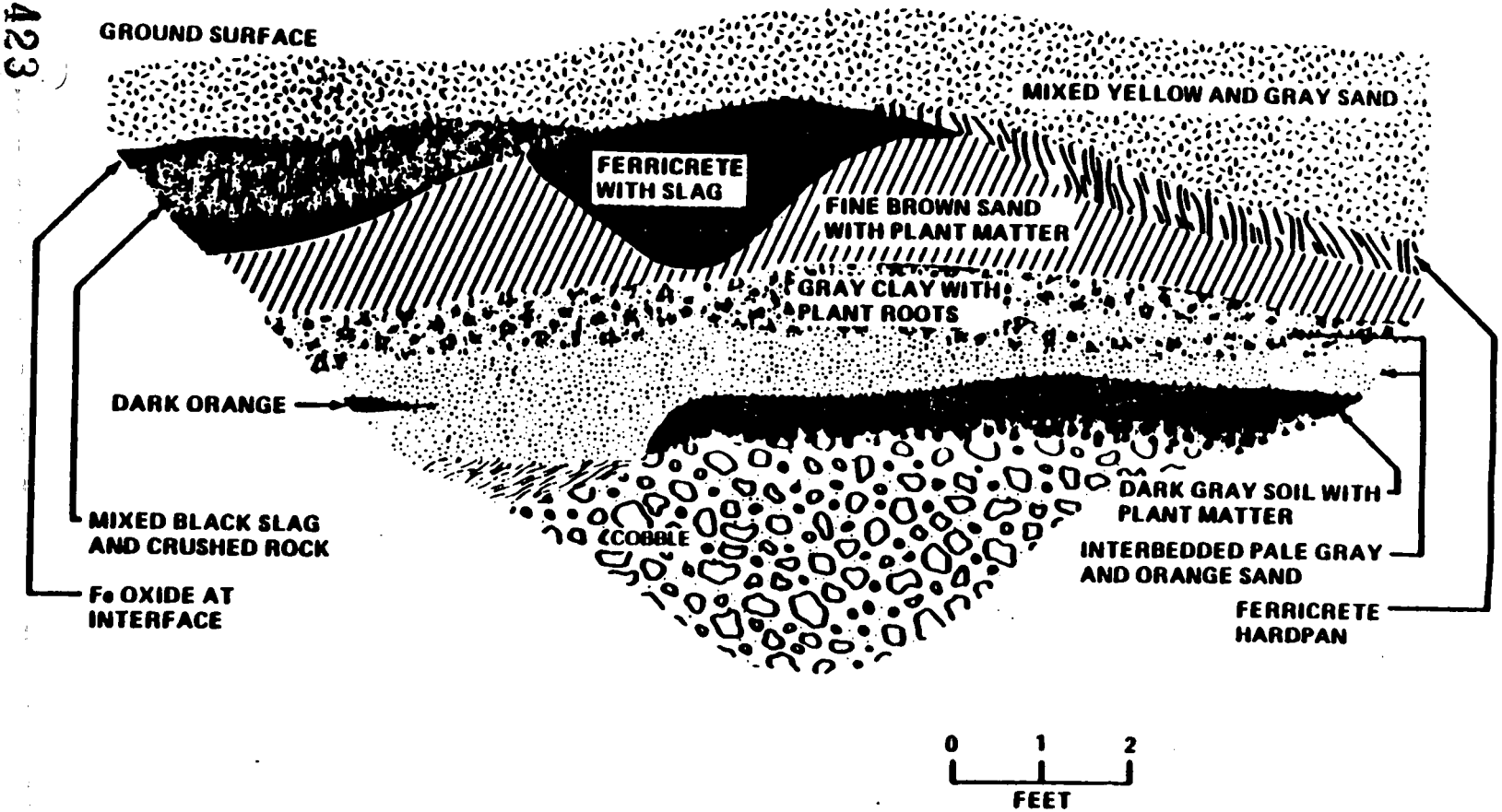
Figure 15-10. Changes in Sulfate Over Time at Selected Wells Located Within the Site

To identify leachate and soil interactions beneath a waste site, trenches may be dug. The trench walls are then logged and photographed. Detailed sampling may be done at closely spaced intervals to confirm that reactions such as precipitation have occurred. Figure 15-11 shows a cross-section of a tailings deposit that was developed based on a trench excavated through the tailings into the underlying alluvium. The plot shows the demarcation between wastes and natural alluvium.

Figure 15-12 shows the details of the chemical composition of one borehole through the tailings and into the underlying alluvium. The chemical composition is shown to vary significantly with depth. These types of plots contain a wealth of chemical information that can help to explain the geochemical processes operative in the tailings. Figure 15-12 also shows the marked contrast between the composition of the tailings (in the top 16 feet) and the underlying alluvium.

Summary

The graphical presentations illustrated in this case study are a few of the many techniques available. With the proliferation of graphical packages available on microcomputers, scientists and engineers have a wide range of tools available for data presentation. Some of these tools are summarized in Table 15-6.



Notes: A BLUE-GREEN PRECIPITATE FORMED ON THE EXPOSED SURFACE OF TOP 6 INCHES OF ALLUVIUM. THIS PRECIPITATE WAS NOT THERE WHEN TRENCH FIRST DUG.

Figure 15-11. Field Sketch of Tailings Trench T-3

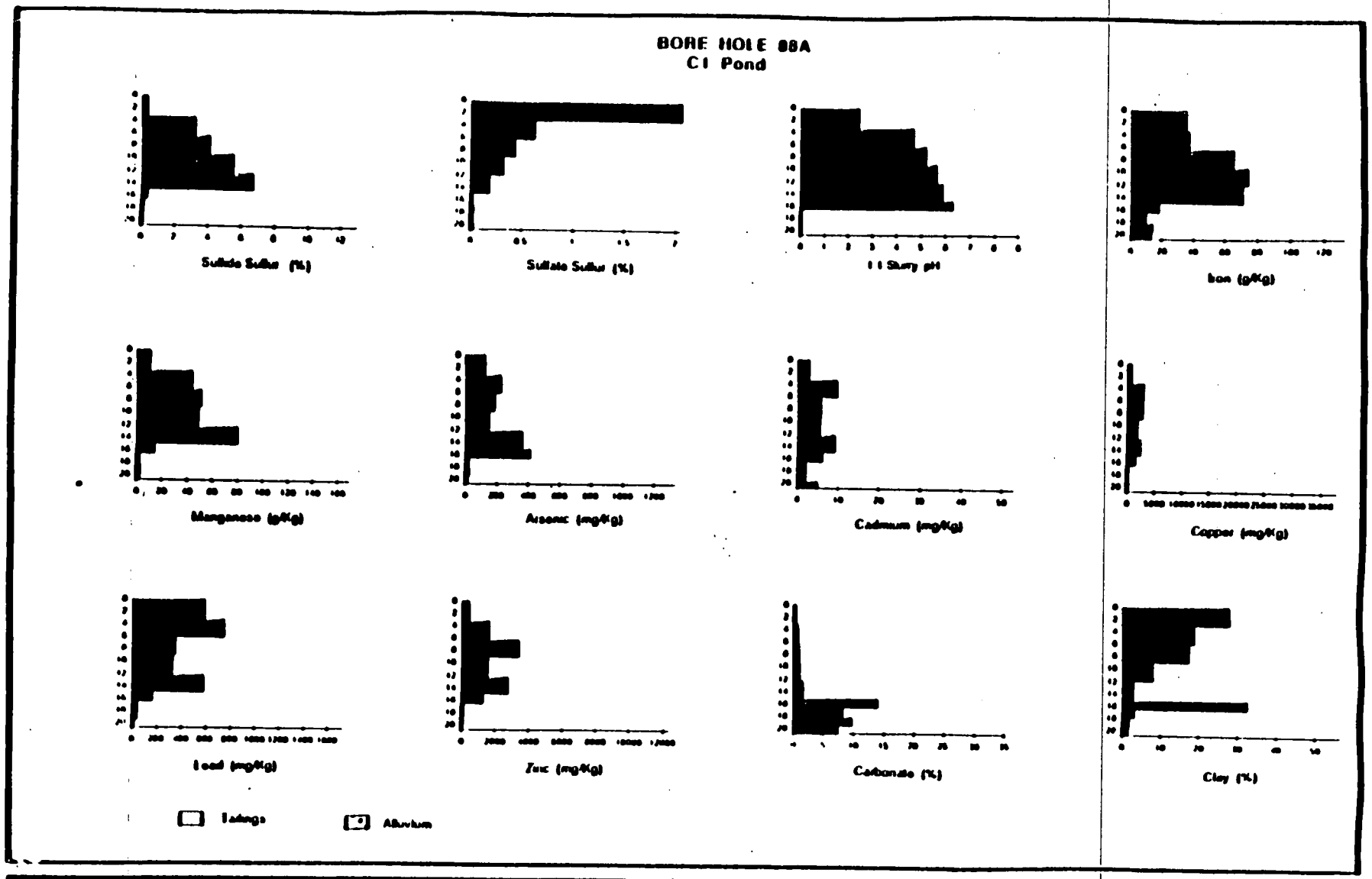


Figure 15-12. Depth vs. Concentration Profiles for Selected Variables for Borehole 88A

TABLE 15-6

TYPICAL METHODS FOR GRAPHICALLY PRESENTING DATA COLLECTED DURING FACILITY INVESTIGATIONS

Data	Graphical Presentation Methods
METEOROLOGIC DATA	
Wind speed and direction	• Wind rose showing speed, direction and percent of observations for each 10° increment
Air temperature	• Bar chart, by month
Precipitation	• Bar chart, by month
Evaporation	• Bar chart, by month
SURFACE WATER DATA	
Flow rates	• Hydrographs; distance profiles, cumulative frequency distributions, flood frequency plots • Hydrologic network depiction and water budgets
Water quality	• Trilinear diagram • Stiff diagrams • Contour showing vertical concentration or temperature variability in two deep water bodies • Time history plots showing daily/annual variability • Bar charts of major cations/anions or contaminants at multiple locations shown on a single map
GEOHYDROLOGIC DATA	
	• Geologic map of site and vicinity • Stratigraphic cross-sections of site in direction of and perpendicular to ground water flow • Well logs • Cross-sections near waste deposits • Solid phase chemical analyses by depth at borings near waste deposits and into alluvium
GROUND-WATER DATA	
	• Water level contours • Flow directions and velocities • Time history of water table at important locations • Stiff diagrams • Trilinear diagrams • Contaminant plumes, showing isopleths
MISCELLANEOUS	
	• Figures with important site features, including waste sources, storage ponds, disposal areas, buildings, sampling locations, well locations • Operational aspects for special sampling equipment (e.g., lysimeters)

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CASE STUDY 7: CORRELATION OF CONTAMINANT RELEASES WITH A SPECIFIC WASTE MANAGEMENT UNIT USING GROUND-WATER DATA

Point Illustrated

- Development of an effective ground-water monitoring program can tie releases of contaminants to specific waste mangement units.

Introduction

Documentation of a release from a specific waste management unit may require the development of a comprehensive ground-water monitoring program coupled with an extensive hydrogeologic investigation. Determination of ground-water flow direction and horizontal and vertical gradients are necessary to assess the direction of potential contaminant migration. Historical data on wastes disposed in specific units can provide information on contaminants likely to be detected downgradient.

Facility Description

Chemicals were manufactured at a 1000-acre facility for over 30 years. The facility produced plastics including cellulose nitrate, polyvinyl acetate, polyvinyl chloride and polystyrenes, and other chemicals such as phenols and formaldehyde. Wastes produced in the manufacturing processes were disposed on site in an unlined liquid waste impoundment and in two solid waste disposal areas. Readily combustible materials were incinerated in four burning pits. Ground-water contamination has been documented at the site. Figure 15-13 shows the facility plan and locations of ground-water monitoring wells.

The site is located in a glacial valley and is adjacent to a major river. A minor tributary runs through the southwestern portion of the facility and drains into the river. Approximately 200 dwellings are located downgradient of the site.

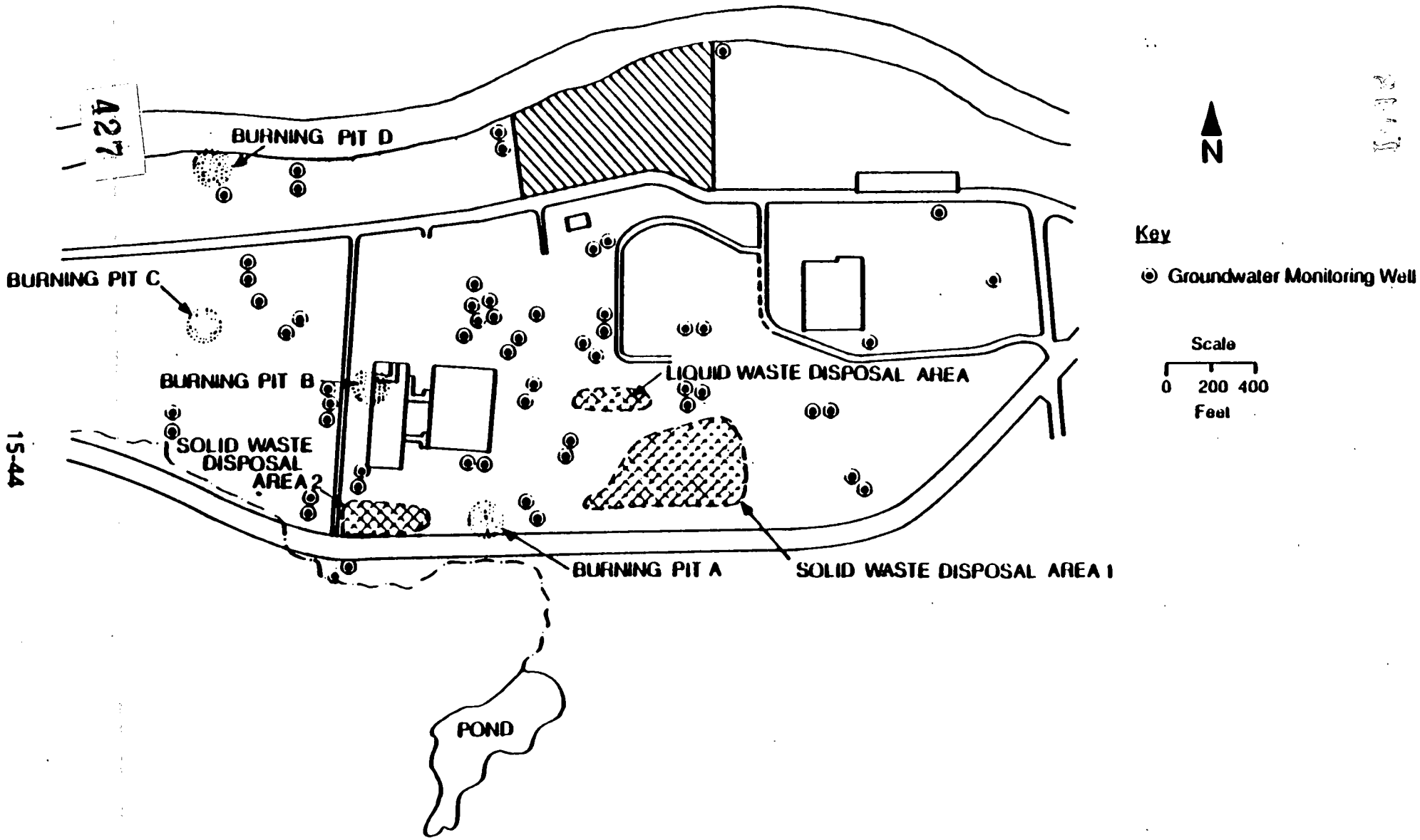

Figure 15-13. Location of Ground-Water Monitoring Wells

Data Collection

Initial studies to assess the extent of ground-water contamination began in 1981. Studies focused on ground water in the vicinity of various waste disposal units. A limited number of monitoring wells were installed in 1983. These wells provided general data on the direction of ground-water flow and chemical constituents that had entered the ground water. In 1984, a two-phased approach was developed to define the areal and vertical extent of contamination and to identify contaminant releases from specific waste management units. The first phase involved the characterization of facility geologic and hydrogeologic conditions using historical data, determination of the chemical nature of contaminants in the ground water using existing monitoring wells, and development of a contaminant contour map delineating the horizontal boundaries of contamination. Based on this data, 33 soil borings were drilled in Phase 2. The goals of the second phase were to: 1) detail subsurface geologic characteristics, vertical and horizontal water flow patterns, contaminant migration, and site-specific chemical contaminants; and 2) install wells that would be used to monitor contaminants being released from all units of concern at the facility.

Continuous split spoon samples were collected in each boring and headspace analyses for volatile organic compounds (VOC) were conducted on each sample. Chemical constituents were identified using a field gas chromatograph. Confirmational analysis by GC/MS were conducted on selected samples. Geotechnical analyses were also conducted on the split spoon samples.

Chemical and hydrogeologic data (direction of flow, gradients) obtained from the borings were used to select appropriate ground-water monitoring well locations and screen depths. Fifty-two (52) nested monitoring wells were installed at 25 locations upgradient and downgradient of each waste management unit, and near the river and its tributary. Screen depths were determined by the depth of maximum VOC contamination observed in the borings and the permeability of soil layers.

Data Analysis

Ground-water contamination data from new wells coupled with historical waste disposal data allowed releases from three specific waste management areas to be defined. Sample analyses showed organic solvents in nearly all locations. However, more unusual constituents associated with specific manufacturing processes were detected in some samples, allowing them to be correlated with releases from specific waste management units. The two situations below illustrate how these correlations were accomplished:

1) PCBs detected in some samples were correlated with Solid Waste Disposal Area #1. This area received construction debris, resins, plastics, metals, drums, and PCB containing transformers. Records indicated that this unit was the only location where transformers were disposed onsite. PCBs could not be associated with any of the other waste management units.

2) The solvent dimethylformamide (DMF) detected in some samples was correlated with Burning Pit B. It was discovered that the building that housed this unit had been used to tint windshields and that DMF is a component of the dye used in this process. DMF could not be tied to any of the other waste management units. A leachfield in which waste dyes had been disposed was discovered under the building and the contamination was traced back to that source.

Case Discussion

An extensive hydrogeologic investigation of the facility was completed and, in conjunction with historical data, was used to develop a comprehensive ground-water monitoring program. Placement of the monitoring wells and screens was essential in providing data that unequivocally linked contaminant releases to specific waste management units and manufacturing processes.

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CASE STUDY 8: WASTE SOURCE CHARACTERIZATION FROM TOPOGRAPHIC INFORMATION

Points Illustrated

- Mapping of changes in site topography can support the selection of locations for test borings and monitoring wells.

- This technique is especially useful at sites where large volumes of waste have been disposed of over several years.

Introduction

Topographic surveys conducted prior to and at different times during the operation of a waste management facility can be used to help characterize the vertical and horizontal extent of waste disposal areas. Because the resolution of this technique is limited, it is most useful when large volumes of waste are involved.

Facility Description

This facility is the same as discussed in Case Study 7 above.

Topographic Survey

In 1984, a topographic survey measuring elevations in feet relative to mean sea level was conducted for the areas shown in Figure 15-14. These elevations were plotted on a map of appropriate horizontal scale and contoured in 2-foot intervals. This topography was transferred to an existing site plan (horizontal scale 1" to 200'). Topographic maps from 1935 (showing the natural topography before waste deposition) to 1960 (showing the topography in the earlier stages of the facility operation) were compared to the 1984 map. By examining the changes in elevations which occurred over time, contours were developed showing the estimated changes in vertical and horizontal units of the liquid waste and solid waste disposal areas.

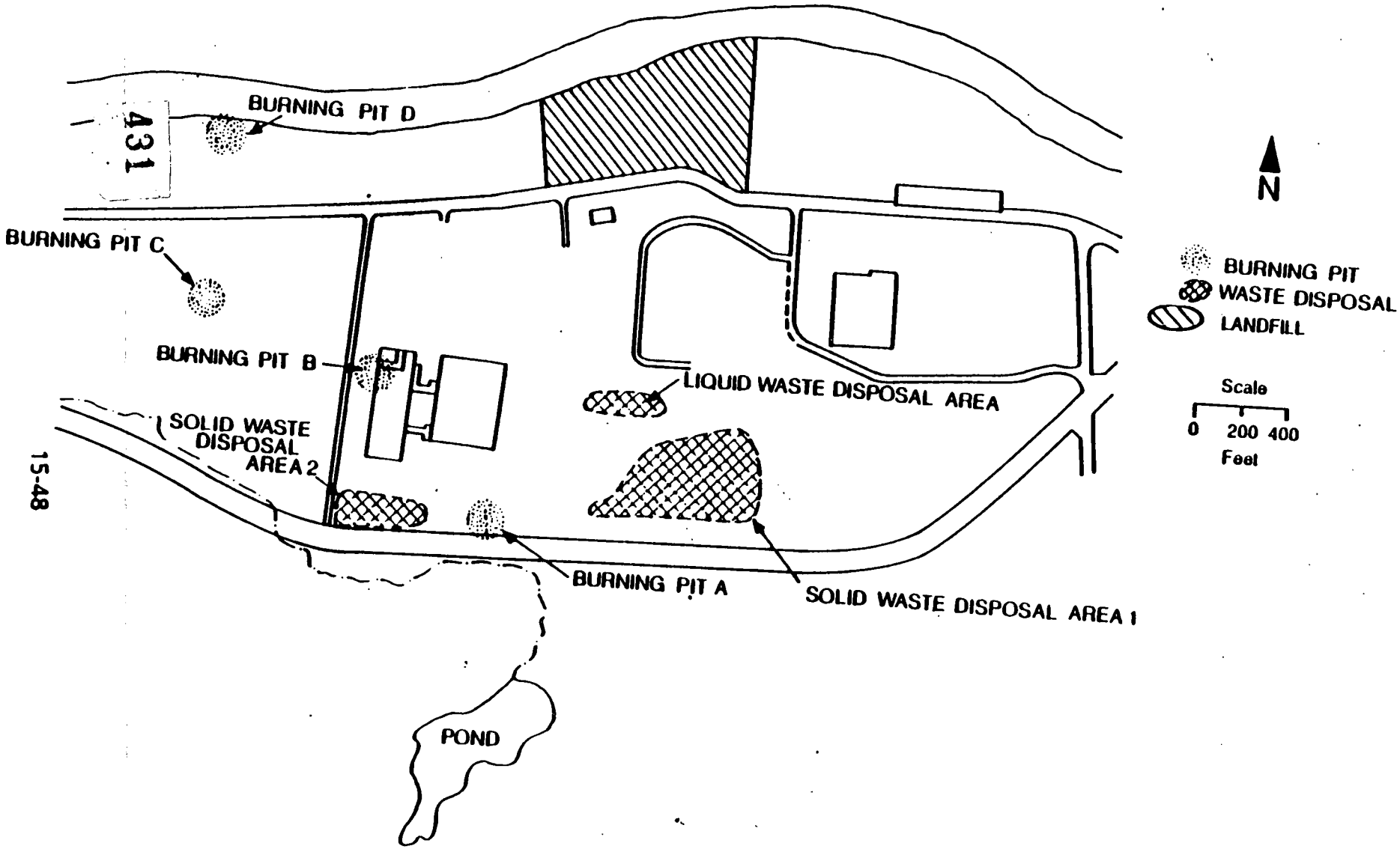

Figure 15-14. Site Map Showing Waste Disposal Areas

Results

From the analysis, it was apparent that the deepest portion of Solid Waste Disposal Area (SWDA) No. 1 (Figure 15-14) was approximately 48 feet, and the Liquid Waste Disposal Area (LWDA) was approximately 30 feet deep. The horizontal limits of the disposal areas were also defined in part by this review, but other field surveys provided more accurate information on the horizontal boundaries of the waste disposal areas.

Case Discussion

Topographic surveys can provide useful information for characterizing disposal areas. The results of these studies can facilitate the selection of appropriate test boring locations, and may reduce the number of borings necessary to describe the subsurface extent of contamination. It should be noted that techniques such as infrared aerial photography and topographic surveying are approximate in their findings. They are useful methods in the early phases of an investigation, but do not replace the comprehensive characterization of the environmental setting needed for the full investigation.

CASE STUDY 9: SELECTION OF GROUND-WATER MONITORING CONSTITUENTS AND INDICATOR PARAMETERS BASED ON FACILITY WASTE STREAM INFORMATION

Points Illustrated

- Waste stream information can be used to identify potential contaminants, and thus to select appropriate ground-water monitoring constituents and indicator parameters.

- The number of initial monitoring constituents analyzed may be significantly reduced from the 40 CFR Part 261 Appendix VIII list when detailed waste stream information is available.

Introduction

Hazardous waste treatment, storage, and disposal facilities subject to RCRA are required to identify all waste streams managed the facility, waste volumes, concentrations of waste constituents, and the waste management unit in which each waste type is disposed. Ground-water monitoring programs should be developed to adequately monitor contaminant migration from each unit. Constituents to be analyzed in the ground-water monitoring program should be established prior to sample collection. When waste stream data are not available, the full set of Appendix VIII monitoring constituents may be required to characterize ground-water contamination. Knowledge of the waste streams managed by a facility simplifies the selection of monitoring constituents and indicator parameters because potential contaminants and their likely reaction and degradation products can be more easily identified.

Facility Description

The 600-acre facility is a permitted waste disposal site operated since 1980. Solid waste management units occupy 20 acres of the site and include four surface impoundments and one container storage area subject to RCRA. Until 1985, three units (two surface impoundments and one solids disposal unit) not subject to RCRA were used for geothermal waste disposal. However, the two surface impoundments

were replaced by a RCRA regulated landfill. RCRA wastes managed by the facility include metals, petroleum refining wastes, spent non-halogenated solvents, electroplating wastewater treatment sludge, spent pickle liquor from steel finishing operations, and ignitable, corrosive, and reactive wastes. Ground-water monitoring wells have been installed downgradient of each waste mangement unit.

Program Design

Prior to disposal, each load of waste received is analyzed in an on-site laboratory to provide a complete characterization of waste constituents. Periodic sampling of the waste management units is also conducted to identify waste reaction products and hazardous mixtures. Even though the incoming wastes have been characterized, the facility owner also analyzed initial ground-water samples from each monitoring well for all Appendix VIII constituents. The resulting data were used to establish existing concentrations for each constituent and to select a set of monitoring constituents and indicator parameters to identify migration of waste to the ground-water system. Table 15-7 includes a list of the indicator parameters analyzed at the facility. Rationale for indicator parameter selection are included in this table. A separate list of hazardous constituents to be monitored was also developed based on the waste analysis.

Because the facility accepts only a limited number of 40 CFR Part 261 Appendix VIII constituents and initial monitoring verified the absence of many constituents, the facility owner or operator was able to minimize the total number of constituents monitored in ground water. The process of constituent elimination is dependent on the actual wastes received by the facility and the physical and chemical properties of these constituents that influence their migration potential (e.g., octanol/water partition coefficients, solubility, adsorptivity, susceptiblity to biodegradation).

Non-halogenated solvents have relatively low partition coefficients (K_{ow}: benzene = 100; toluene = 500) and are not readily retained by soils. Conversely, polycyclic aromatic hydrocarbons, constituents of petrochemical wastes, have very high partition coefficients (e.g., chrysene = 4×10^5) and are generally immobile in soils. Migration rates of metals are also influenced by the exchange

TABLE 15-7

INDICATOR PARAMETERS

Parameter	Criteria for Selection
Total Organic Carbon (TOC)	Collective measure of organic substances present
Total Petroleum Hydrocarbons	Indication of petroleum waste products
Total Organic Halogen (TOX)	Halogenated organic compounds are generally toxic, refractory, and mobile
Nitrates	Mobile contaminant, degradation product of nitrogen compounds
Chloride	Plating solution constituent, highly mobile in ground water. Early indicator of plume arrival
Sulfides	Toxic, biodegradation by product, strong reducing agent, may immobilize heavy metals
pH	Good indicator of strongly acidic or alkaline waste leachates close to sources
Total phenols	Collective measure of compounds likely to be in waste. Even small concentrations can cause olfactory problems following water treatment by chlorination

capacity of the soil. Different metal species are sorbed to different extents. Following an assessment of the migration potential of each waste constituent, the need for analysis of that constituent can be prioritized.

Case Discussion

Waste stream information was used to determine appropriate monitoring constituents and indicator parameters. The use of the existing initial ground-water quality data and the incoming waste analyses allowed for prediction of contaminants of concern in ground water and reduced the number of constituents requiring analysis.

CASE STUDY 10: USING WASTE REACTION PRODUCTS TO DETERMINE AN APPROPRIATE MONITORING SCHEME

Point Illustrated

- It is important to consider possible waste reaction products when developing monitoring procedures.

Introduction

Volatile organic priority pollutants have been detected in ground water at various areas across the country. These compounds, widely used as solvents, are generally considered environmentally mobile and persistent. Increasing evidence, however, indicates that chlorinated solvents can be degraded under anaerobic conditions by reductive dehydrochlorination. The sequential removal of chlorine atoms from halogenated 1 and 2 carbon aliphatic compounds results in formation of other volatile priority pollutants which can be detected during investigations of solvent contamination.

Facility Description

The facility is a small municipal landfill sited on a former sand and gravel quarry. In addition to municipal wastes, the landfill accepted trichloroethane and tetrachloroethene contaminated sludge from a local fabrication plant until 1975. In 1983, a municipal well located downgradient of the landfill tested positive for dichloroethane, dichloroethene isomers, and vinyl chloride. This prompted the city to investigate the cause and extent of the problem.

Site Investigation

According to records kept at the facility, some of the compounds found in the municipal well were not managed at the facility. This prompted the city to request that a monitoring program be developed to determine whether another source was causing well contamination. A careful search of the city records, however, failed to indicate a credible alternative source of the compounds. Suspecting that the landfill was the source of the well contaminants, five monitoring wells were

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installed (Figure 15-15) and water samples were analyzed for halogenated compounds using EPA Method 601. The results, given in Table 15-8, show an increase in degradation products of trichloroethane and tetrchloroethene with increasing distance from the landfill. Using these data, supported by hydrogeologic data from the monitoring wells, the municipal landfill was shown to be the source of the observed contamination.

TABLE 15-8
RESULTS OF MONITORING WELL SAMPLING

	WELL NUMBER (See Figure 15-15 for well locations)				
	1	2	3	4	5
Chlorinated Ethanes					
(1) Trichloroethanes	10(3)	68	ND(4)	ND	ND
(2) 1,1-Dichloroethane	71	240	130	11	13
1,2-Dichloroethane	ND	12	21	ND	ND
Chloroethane	ND	21	18	160	ND
Chlorinated Ethenes					
(1) Tetrachloroethene	80	13	ND	ND	ND
Trichloroethene	12	100	62	ND	ND
(2) 1,2-Dichloroethenes	ND	990	950	150	ND
1,1-Dichloroethene	ND	ND	ND	ND	ND
Vinyl Chloride	ND	120	59	100	ND

(1) Parent Compounds
(2) Degradation Products
(3) All Concentrations In Micrograms/L
(4) ND means < 10 Micrograms/L

Case Discussion

Based on the compounds found in the municipal well, the city believed that the municipal landfill could not be the source of the contamination. If this reasoning had been followed, then a system of monitoring wells might have been needlessly installed elsewhere in the attempt to find an alternate source of the

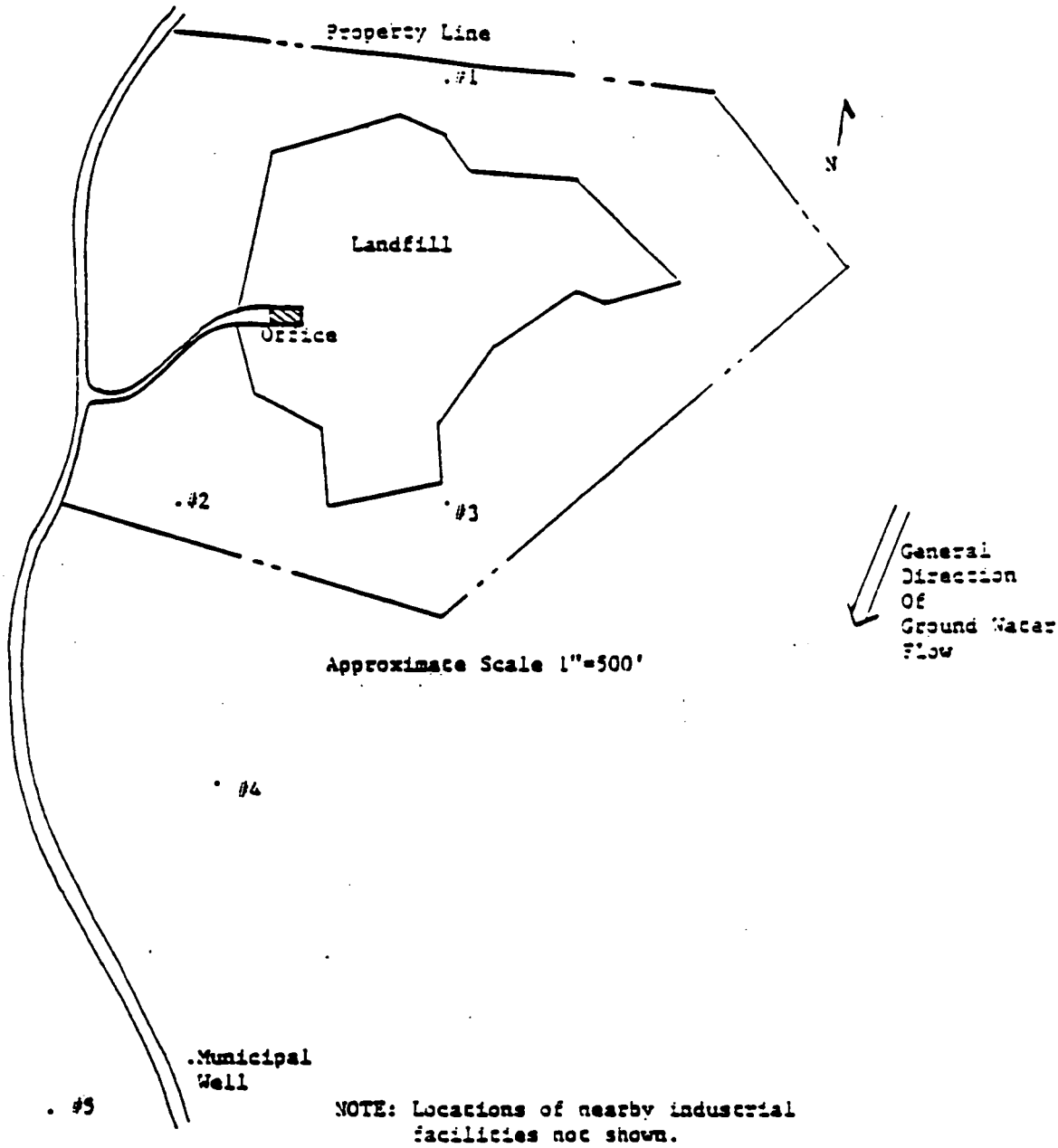

Figure 15-15. Site Map and Monitoring Well Locations

contamination. Instead, after carefully researching local industries, it was determined that the landfill was the most reasonable source of the contamination and that the observed well contaminants were probably degradation products of the landfilled solvents. The progressive dehalogenation of chlorinated ethanes and ethenes, as shown in Table 15-8, is commonly encountered in situations where chlorinated solvents are subjected to anaerobic conditions (Wood, 1981). Different degradation reactions may occur when pesticides are subjected to acidic or alkaline conditions or biological degradation. Therefore, it is important to keep reaction products in mind when designing any monitoring scheme or interpreting contamination data.

Reference

Wood, P.R., R.F. Lang, I.L. Payan, and J. DeMarco. 1981. Anaerobic Transformation, Transport and Removal of Volatile Chlorinated Organics in Ground Water. First International Conference on Ground Water Quality Research, October 7-10, 1981, Houston, Texas.

CASE STUDY 11: CORRECTIVE MEASURES STUDY AND THE IMPLEMENTATION OF INTERIM MEASURES

Points Illustrated

- Interim corrective measures may be necessary to protect human health or the environment.
- The evaluation of the need for definitive corrective measures.

Introduction

The development and implementation of a comprehensive Corrective Measures Study can be a time-consuming process. Between the time of the identification of a contaminant release and the completion of definitive corrective measures, existing conditions or contaminant migration can endanger human health or the environment. Under such conditions interim measures may be necessary. The case study presented below illustrates the implementation of interim measures to reduce contaminant migration and to remove the imminent threat to the nearby population from exposure to contaminants in drinking water, and also illustrates the decision- making process as to whether definitive corrective measures may be necessary.

Facility Description

The facility in this case study is an underground tank farm located at a pharmaceutical manufacturing plant. The tank farm encompasses an area approximately 140 feet by 260 feet and contains 30 tanks ranging in size from 12,000 to 20,000 gallons. The tanks are used to store both wastes and raw materials for the various batch manufacturing processes performed at the plant. Typical wastes include carbon tetrachloride, acetonitrile and chloroform. At the time of the release, the tank farm had no cap to prevent the infiltration of rainfall or runoff. It also did not have berms to provide containment for surface spills. No leak detection or leachate collection systems were present.

Geological and Hydrological Setting

The site is underlain by silty soil overlying limestone. The weathered limestone beneath the site is very permeable (up to 210 ft/day) due to the solution of rock along joints and bedding planes in the limestone. Depth to the limestone varies from 3 to 80 feet beneath the tanks and from 15 to 190 feet downgradient of the site.

The ground-water system beneath the site consists of two aquifers. The upper one, an unconfined limestone aquifer, is about 300 feet below the surface. The deep aquifer is an artesian aquifer in another limestone formation about 1200 feet below the land surface. Ground-water flow in the upper aquifer is controlled by both the regional flow system and local channelized flow through solution conduits. The upper aquifer discharges to a canal 3 miles north of the site. Figure 15-16 shows the ground-water elevation contours in the vicinity of the site. Regional average ground-water flow velocity was estimated at 4 ft/day, but ground-water velocities on the order of 50 ft/day have been measured in some channelized areas. Channelized flow is also responsible for local deviations in flow direction.

Release Characterization

A contaminant release from the tank farm was discovered when one of the tanks used for waste storage was found to be empty. The waste stored in the tank was predominately carbon tetrachloride (CCl_4) (a carcinogen with an MCL of 0.005 mg/l, with some acetonitrile (a systemic toxicant with a water-based health criterion of 200 µg/l) and chloroform (a systemic toxicant with a water-based health criterion of 400 µg/l) reference dose (RfD) is 0.4 mg/l). Approximately 15,000 gallons of waste liquids had been routed to the tank before the leak was discovered. Excavation of the tank revealed ruptures in at least three locations. Initial ground-water monitoring after the tank rupture was discovered identified CCl_4 in a well 2500 feet downgradient of the site, at concentrations above the MCL for CCl_4 of 0.005 mg/l.

Contaminants from the leaking tank were found to have dispersed laterally within a two-foot-thick sand bed which underlies the tanks. The contaminated area

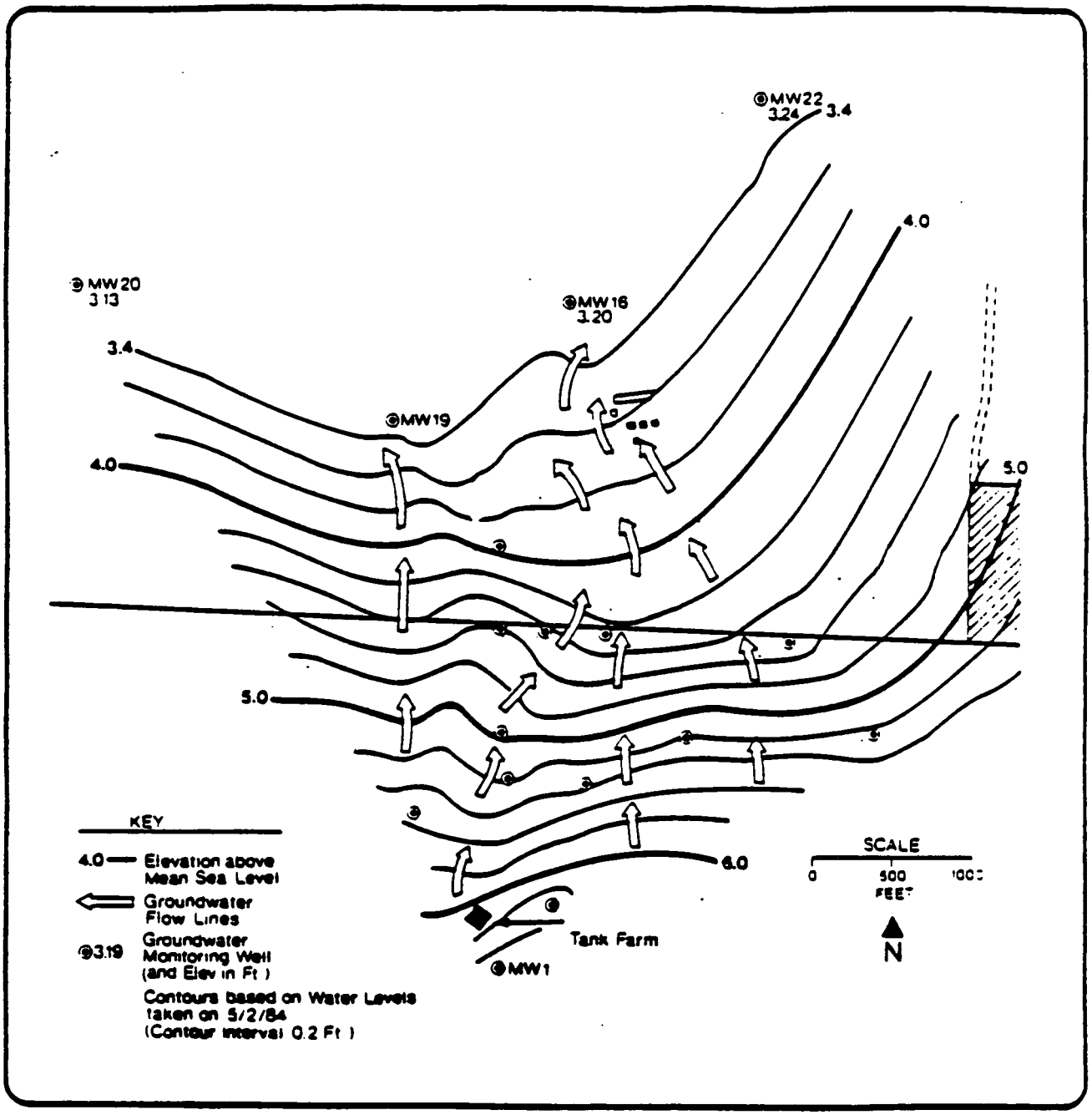

Figure 15-16. Ground-Water Elevations and Flow Directions in Upper Limestone Aquifer

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was approximately 5600 ft^2. High levels of CCl_4 were found throughout the sand layer. Concentrations of CCl_4 in the natural soil ranged between undetected and 2200 mg/kg. Observed concentrations were well above the soil RSD for CCl_4 (2.7 mg/kg). Concentrations generally decreased with depth due to adsorption onto the clay particles in the soil. Carbon tetrachloride apparently moved downward with little lateral dispersion until reaching the soil-limestone interface. Upon reaching the unsaturated limestone, the contaminants then appeared to have rapidly dispersed over an area of about 12 acres before entering the aquifer.

Interim Corrective Measures

Immediate action to contain the release in the aquifer was taken. This involved pumping the well where CCl_4 had been found continuously at its full capacity of 450 gpm.

All drinking water in the vicinity of the release was obtained from wells installed in either the shallow or artesian aquifer. Immediately after the detection of the release, all domestic and industrial wells north of the facility were tested for CCl_4 contamination. Test results showed contamination of several shallow water supply wells. Based on this information and the inferred ground-water flow direction to the north-northeast, wells serving two small communities and a nearby motel were closed. The facility operator hired all mobile water tanks available and supplied water for immediate needs until a temporary water supply could be implemented. Water from an unaffected artesian well was then used to supply water to these communities.

The design and operation of the tank farm was altered in an attempt to avoid similar problems in the future. A fiber-reinforced concrete cap was installed over the tank farm to prevent the infiltration of rainfall and runoff, thus minimizing further contaminant migration in the soil. The ruptures were repaired, and a tank monitoring system was also developed and implemented at the site.

Definitive Corrective Measures: Saturated and Unsaturated Zones

A comparison of CCl_4 concentrations within the ground water to the MCL for CCl_4 (0.005mg/l) indicated that definitive corrective measures may be necessary.

Due to the high mobility of CCl_4 within the unsaturated zone, and the potential for continued inter-media transfer from this zone to the ground water, definitive corrective measures for both the saturated (ground water) and unsaturated zones should be evaluated in a Corrective Measures Study (CMS).

Case Discussion

The development and implementation of definitive corrective measures at a site may take a substantial length of time. Depending on the nature and severity of the release and the proximity of receptors, interim measures, such as alternative water supplies, were required to minimize the effects on human health and the environment. Comparison of constituent concentrations with health and environmental criteria indicated that definitive corrective measures may be necessary and that a Corrective Measures Study (CMS) should be initiated.

CASE STUDY 12: USE OF AERIAL PHOTOGRAPHY TO IDENTIFY CHANGES IN TOPOGRAPHY INDICATING WASTE MIGRATION ROUTES

Points Illustrated

- Aerial photographs can be used to obtain valuable data on facility-related topographic features, including type of waste management activity, distance to residences and surface waters, adjacent land use, and drainage characteristics.

- Detailed interpretation of aerial photographs can identify actual and potential waste migration routes and areas requiring corrective action.

Introduction

Stereoscopic pairs of historical and current aerial photographs were used to assist in the analysis of waste management practices at a land disposal facility. Stereo viewing enhances the interpretation of aerial photographs because vertical as well as horizontal spatial relationships can be observed, and because the increased vertical resolution aids in distinguishing various shapes, tones, textures, and colors within the study area. Typical items that should be noted include pools of unknown liquid that may have been released from buried materials which could migrate off site through drainage channels. Soil discoloration, vegetation damage, or enhanced vegetation growth can also be indicative of contaminant migration.

Facility Description

The site contains an active land disposal facility which receives bulk hazardous waste, including sludges and contaminated soil for burial, and liquid wastes for disposal into solar evaporation surface impoundments. Operations at the facility began in 1969. Historical and current aerial photographs were reviewed to assess waste management practices and to identify potential contaminant migration pathways requiring further investigation and corrective action.

Data Collection and Anaysis

Low altitude color aerial photographs of the facility (scale = 1:8400) were obtained in October 1983 and Feburary 1984. The photos were interpreted by an aerial photo analyst at the U.S. EPA Environmental Monitoring and Support Laboratory at Las Vegas, Nevada. Figure 15-17 shows the analyzed photograph. The interpretation code is given in Figure 15-18. Analysis of the photograph indicates several areas of seepage at the base of the surface impoundments. This seepage indicates that either the impoundments are not lined or the liners have failed. Drainage from the western portion of the facility which contains most of the impoundments flows into a drainage reservoir formed by a dam across the main drainage. Drainage from the northeast portion of the facility where seepage was also observed appears to bypass this reservoir and enter the main drainage which flows offsite. Besides possible surface contamination, this seepage also indicates potential subsurface contamination.

The aerial photograph obtained in February 1984 (Figure 15-19) indicates the continued existence of seepage from the surface impoundments. There is evidence of possible discharge from the drainage reservoir to a stream channel, as a pump and piping were observed. Additional material in the solid waste disposal area has altered the drainage pattern. At the south end of this area, seepage is evident in association with damaged vegetation. Drainage from this area enters a drainage system and appears to be diverted offsite.

Case Discussion

Analysis of aerial photographs of the land disposal facility enabled investigators to identify potential contaminant sources and migration pathways. This information was used by investigators to identify areas for surface water, sediment, soil, and subsurface sampling.

Figure 15-17. October 1983 Aerial Photograph of Land Disposal Facility

INTERPRETATION CODE

BOUNDARIES AND LIMITS

- FENCED SITE BOUNDARY
- UNFENCED SITE BOUNDARY
- FENCE
- PROPERTY LINE
- GATE/ACCESS POINT
- SECTION CORNER

DRAINAGE

- DRAINAGE
- FLOW DIRECTION
- INDETERMINATE DRAINAGE

TRANSPORTATION/UTILITY

- VEHICLE ACCESS
- RAILWAY
- PIPELINE
- POWERLINE

SITE FEATURES

- DIKE
- STANDING LIQUID
- SL — STANDING LIQUID (SMALL)
- EXCAVATION, PIT (EXTENSIVE)
- MOUNDED MATERIAL (EXTENSIVE)
- MM — MOUNDED MATERIAL (SMALL)
- CR — CRATES/BOXES
- DR — DRUMS
- HT — HORIZONTAL TANK
- PT — PRESSURE TANK
- VT — VERTICAL TANK
- CA — CLEARED AREA
- DG — DISTURBED GROUND
- FL — FILL
- IM — IMPOUNDMENT
- LG — LAGOON
- OD — OPEN DUMP
- OF — OUTFALL
- SD — SLUDGE
- ST — STAIN
- SW — SOLID WASTE
- TR — TRENCH
- WO — WASTE DISPOSAL AREA

449 Figure 15-18. Aerial Photograph Interpretation Code

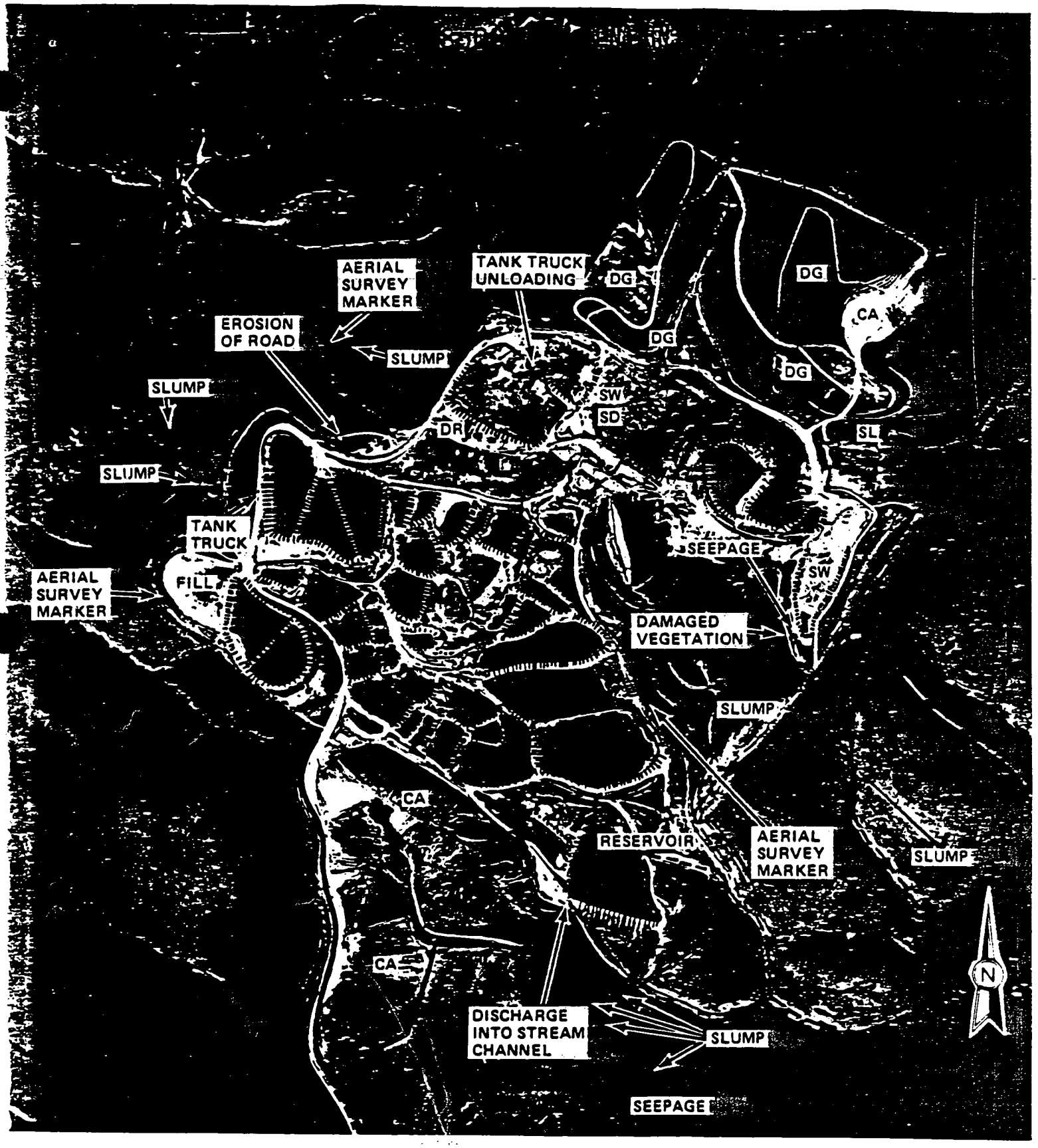

Figure 15-19. February 1984 Aerial Photograph of Land Disposal Facility

CASE STUDY 13: IDENTIFICATION OF A GROUND-WATER CONTAMINANT PLUME USING INFRARED AERIAL PHOTOGRAPHY

Point Illustrated

- Infrared photography can assist in identifying contaminant plumes and in locating monitoring wells by showing areas of stressed vegetation and contaminated surface water.

Introduction

Infrared aerial photography can assist in identifying contaminant plumes at sites where little or no monitoring has been conducted. By identifying areas of stressed vegetation or contaminated surface water, it may be possible to focus on contaminant discharge points and roughly define the extent of a release. Hydrogeologic investigations and surface water sampling can then be performed to further characterize the release. Infrared photography offers the potential to increase the efficiency of a sampling program.

Facility Description

The facility is a municipal solid waste landfill which has served a population of 22,000 for 30 years. The facility covers an area of 11 acres, holding an estimated 300,000 tons of refuse. The majority of waste in the landfill was generated by the textile industry. Until July 1978, the facility was operated as an open dump with sporadic management. City officials indicated that original disposal occurred in open trenches with little soil cover. After July 1978, the facility was converted to a well-operated sanitary landfill. Figure 15-20 shows the facility.

Geologic Setting--

The landfill is located on a sandy to silty till varying in thickness from 23 feet at the hill crest to 10 feet on the side slope. A swamp is present at the base of the hill at about 255 feet above sea level. There is a dam at the southern drainage outlet

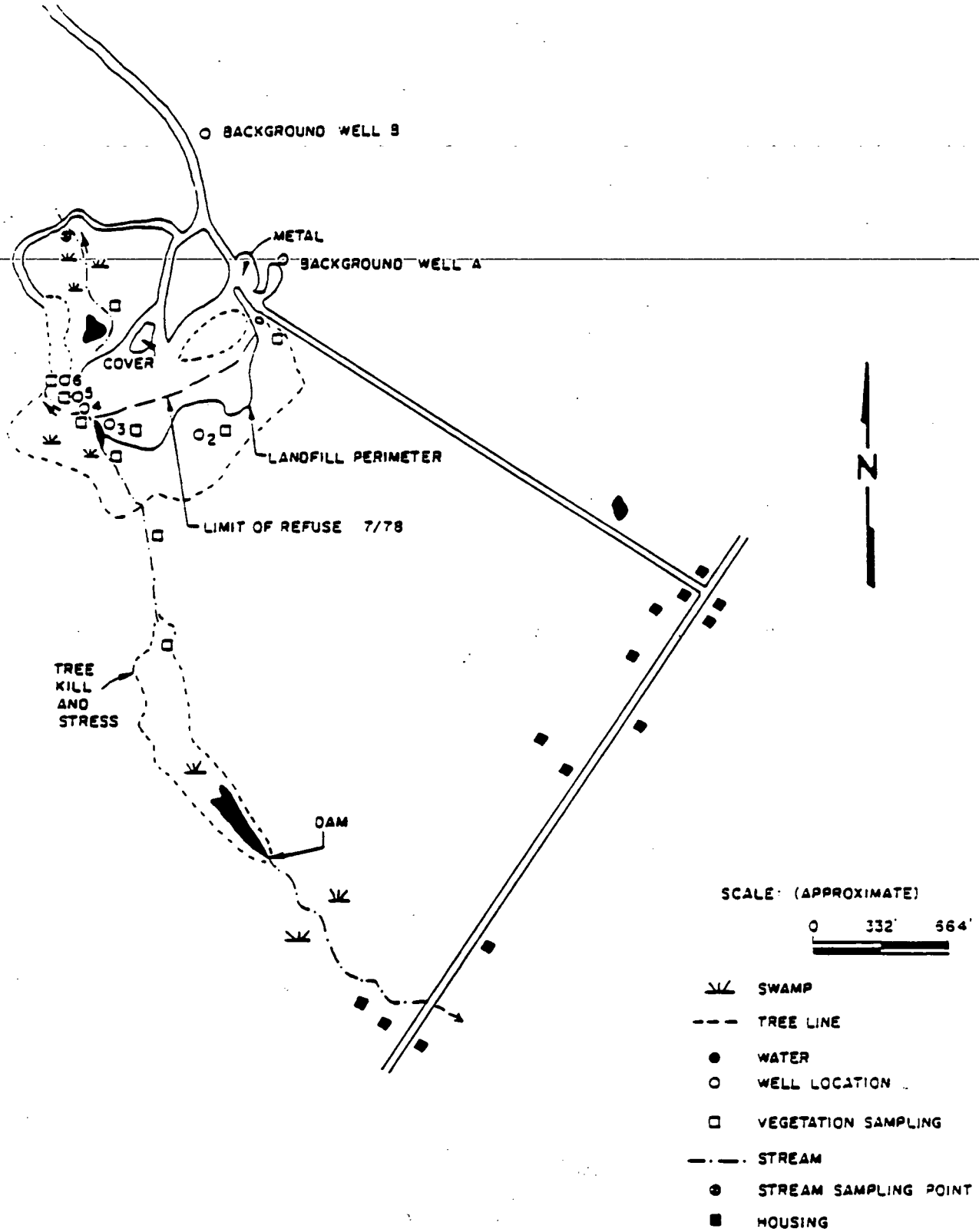

Figure 15-20. Facility Plan View

of the swamp, a distance of 2,500 feet from the landfill. Ground water is approximately 20 feet below the surface at the crest of the hill, while on the slope it is approximately 6 feet below the surface. The swamp at the foot of the hill is the surface expression of the ground water (Figure 15-21).

Aerial Photography and Sampling Program

Figure 15-22 shows the infrared aerial image of the site. The landfill corresponds to the light area in the northwest portion of the photograph (Figure 15-21). The dark area to the south of the site is stressed vegetation, and the light area within it is contaminated swamp water. The 33-acre area of tree kill and stress is clearly visible in the original photograph. Plants under stress may be detected by infrared photography because of changes in infrared reflectance.

Ground-water monitoring wells and vegetation sampling points are shown in Figure 15-20. Data collected from the wells indicated elevated levels of chromium, manganese, iron, and total organic carbon (TOC). Table 15-9 lists the average concentrations of the parameters tested. The vegetation study indicated an accumulation of heavy metals.

Case Discussion

The vegetative stress apparent in the infrared photography was confirmed by the data from the ground water and vegetation sampling. However, the site requires further characterization to determine the vertical extent of contamination and to assess the potential for impact beyond the present area of stressed vegetation.

It should be emphasized that infrared photography is not a substitute for hydrogeologic characterization. However, it is a useful tool for identifying areas of stressed vegetation that may be associated with releases from waste disposal sites.

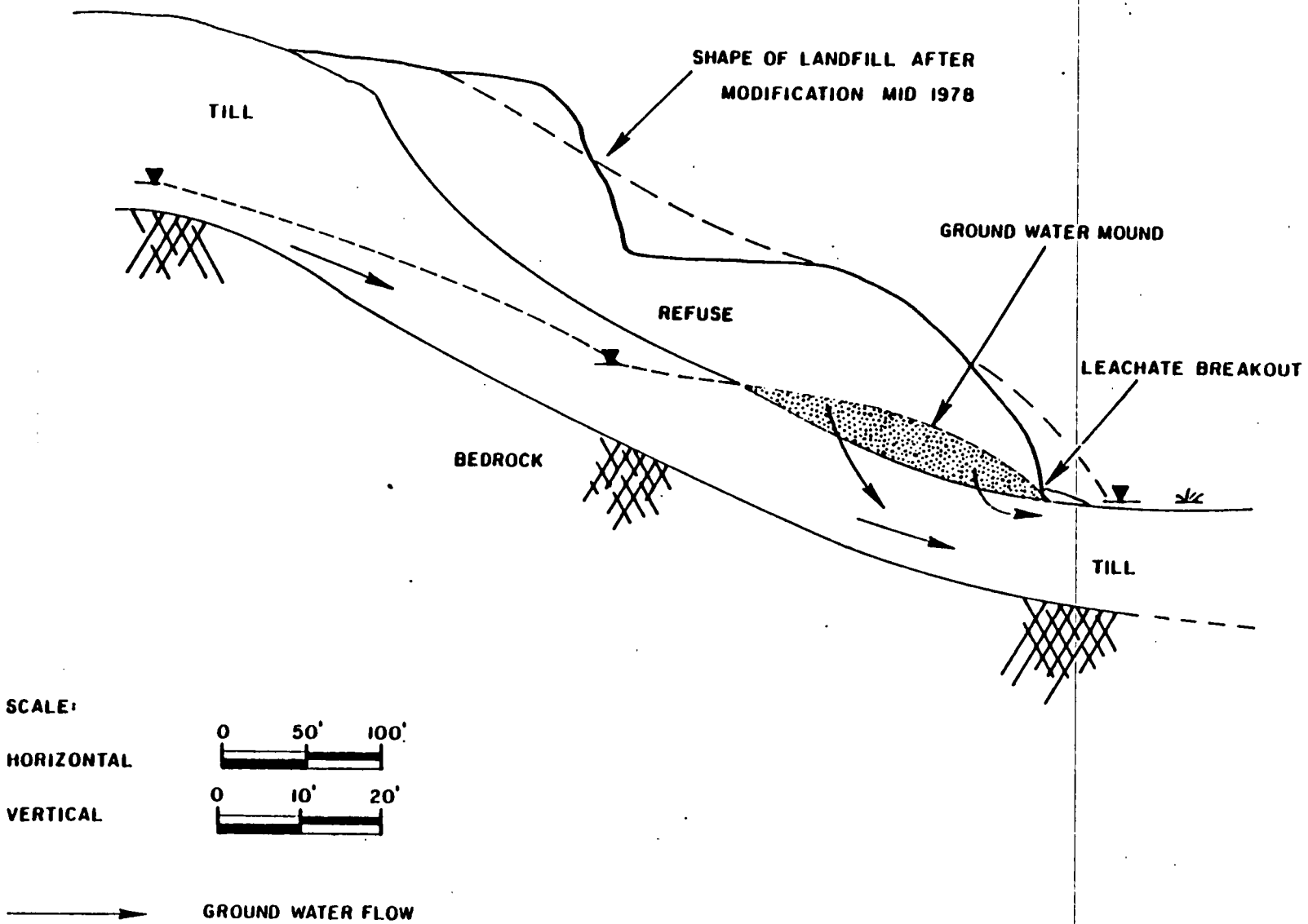

Figure 15-21. Generalized Geologic Cross-Section

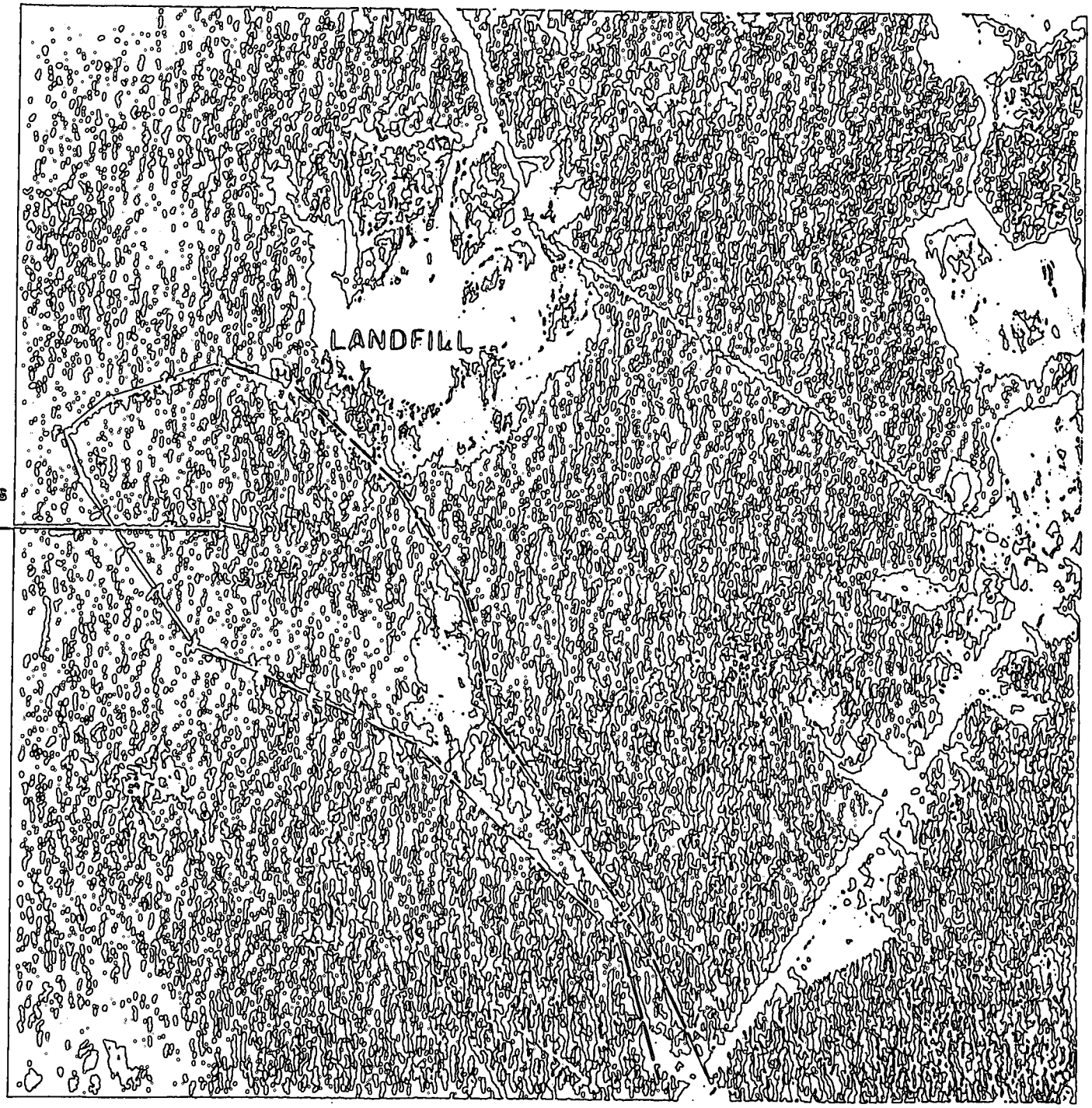

Figure 15-22. Infrared Aerial Photograph of the Site

TABLE15-9

AVERAGE VALUES OF PARAMETERS IN GROUND WATER AND STREAM SAMPLES[1]

	BOD_5	TOC	TKN	NH_3	NO_3 =	Tot.P	Fe	Mn	Hardness	Cl	ClBD	Cr	TDS	Cd	pH
Background[2]	<10	/	/	/	/	1.73	2.7	0.4	18.2	5.2	102	/	98	0.05	/
Well #2	<20	119	1.7	0.54	0.48	0.11	108.8	4.2	525.6	67.3	1000	0.03	828.5	1	2.9
Well #3	<20	56	5.5	3.9	0.10	0.15	39.6	16.3	414.2	103.5	450	0.02	230	---	5.5
Well #4	/	300	2.5	<0.01	<0.01	0.13	27	9.4	1	980		0.02	/	/	5.4
Well #5	20	45.5	0.6	1.22	0.15	0.18	71.6	3.8	353	74.7	240	0.03	863.0	1	5.8
Well #6	19	45.5	3.4	2.47	<0.1	1.5	177	7.65	659.9	120	1300	0.71	780	/	5.7
Stream	<20	72.5	43.7	49.7	0.05	0.10	18.4	1.73	230	76.7	1300	0.017	817	/	6 8

1 All values as mg/l, except conductivity (μmhos) and pH (standard units)
2 Average of background wells A and B
/ = Not Analyzed

CASE STUDY 14: USE OF HISTORICAL AERIAL PHOTOGRAPHS AND FACILITY MAPS TO IDENTIFY OLD WASTE DISPOSAL AREAS AND GROUND-WATER FLOW PATHS

Points Illustrated

- Aerial photographs taken over many years in the life of a facility can be used to locate old solid waste management units (SWMUs).

- Historical aerial photographs can be used to identify geologic/topographic features that may affect ground-water flow paths.

Introduction

In gathering information pertaining to investigation of a release, historical aerial photographs and facility maps can be examined and compared to current aerial photographs and facility maps. Aerial photographs can be viewed as stereo pairs or individually. Stereo viewing, however, enhances the interpretation because vertical as well as horizontal spatial relationships can be observed. The vertical perspective aids in distinguishing various shapes, tones, textures, and colors within the study area.

Aerial photographs and facility maps can be used for the following:

- Providing evidence of possible buried drums. Historical photographs can show drums disposed of in certain areas where later photographs show no indications of such drums, but may show that the ground has been covered with fill material.

- Showing previous areal extent of landfill or waste management area. Earlier photographs might show a much larger waste management area than later photographs.

- Showing areas that were dry but now are wet, or vice versa, indicating a possible release from an old waste management area.

- Showing changes in land use patterns (e.g., a landfill in an early photograph could now be a park or be covered by buildings).

- Soil discoloration, vegetation damage, or enhanced vegetative growth can sometimes be detected, indicating possible contaminant migration.

- Geologic/hydrologic information, such as faults, fracture or joint systems, old stream courses (channels), and the contact between moraines and outwash plains.

Facility description

This facility is the same as previously described in Case Studies 7 and 8.

Data collection and analysis

Over the past 50 years aerial photographs were taken of the facility area. Interpretation of the photographs produced important information that is shown diagramatically in Figure 15-23. Solid Waste Disposal Area 2 (SWDA-2) was lower in elevation in 1940 than it is now. In fact, the area appears to have been leveled and is now covered by vegetation, making it difficult to identify as a SWMU at ground level. Another area was identified as a possible waste disposal area from a historical review of photos. Further study of photographs, facility maps and facility files revealed this to be a former Liquid Waste Disposal Area (LWDA), designated as LWDA-2 on Figure 15-23.

The use of these historical photographs also revealed geologic features that could affect the ground-water flow system under the facility. In this case, monitoring well data indicated a general northwesterly ground-water flow direction, in addition to a complex flow pattern near LWDA-1 and SWDA-1 (Figure 15-23). Recent photographs were analyzed, but because of construction and other nearby activities (e.g., cut and fill, sand and gravel mining), conclusions could not be drawn. A review and analysis of old photographs revealed the existence of a buried stream channel of the river (Figure 15-23). This buried stream channel was identified as a preferential path for ground water and consequently contaminant

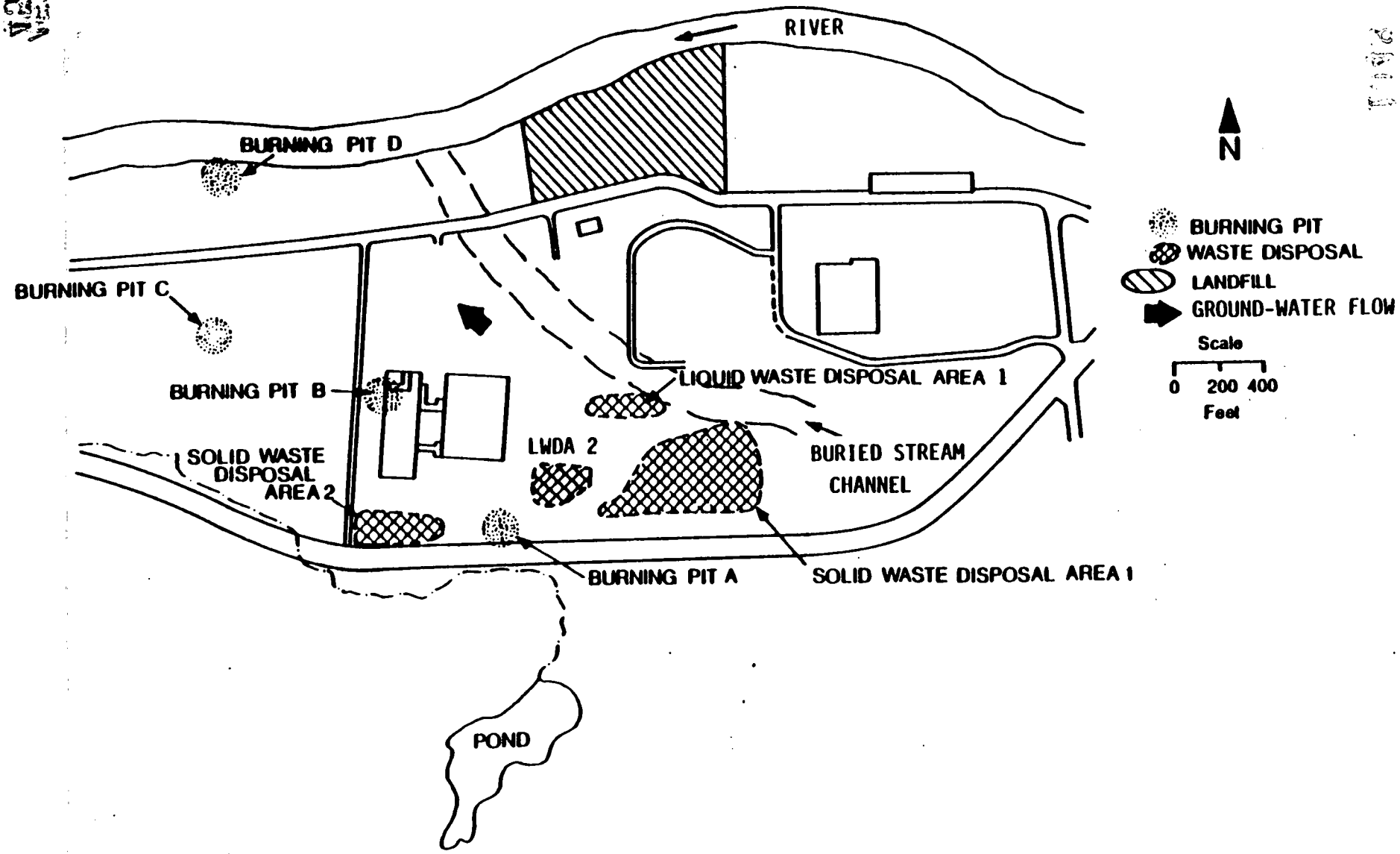

Figure 15-23. Site Layout. LWDA-2, SWDA-2 and Stream Channel Identified Through Use of Aerial Photograph Analysis

migration. Additional monitoring data and further analysis of subsurface geologic data is needed to determine the full impact of the buried stream channel on the ground-water flow regime.

Case Discussion

Analysis and interpretation of a series of historical aerial photographs and facility maps spanning a period of over 50 years enabled facility investigators to identify the following:

(1) Location of waste disposal areas (e.g., old SWMUs);

(2) Changes in topography (related to earlier disposal activities); and

(3) Possible preferential pathways (e.g., old stream channel) for migration of ground water and contaminants.

This information was used to identify areas for more detailed sampling and analysis.

Analysis of historical facility maps and historical aerial photographic interpretation can be a very powerful tool in a RCRA Facility Investigation, but should be used in combination with other investigative techniques to result in a thorough characterization of the nature, extent, and rate of contaminant migration.

CASE STUDY 15: USING SOIL CHARACTERISTICS TO ESTIMATE MOBILITY OF CONTAMINANTS

Point Illustrated

- Information on soil characteristics can be used to estimate the relative mobility of contaminants in the subsurface environment.

Introduction

The relative mobility of contaminants can be estimated using soil characteristics and aquifer hydraulic characteristics. Although metals do precipitate at higher concentrations, at the levels encountered in most subsurface environments, sorption is the dominant attenuation process. The degree to which a metal sorbs onto soil particles depends on the soil pH, the percent clay, the percent soil organic matter, the presence of particular coatings (e.g., iron, manganese, and aluminum oxide/hydroxides) and, to a lesser extent, the type of clay present. For organic contaminants, there are several processes which may be important in predicting their fate in soils. These include sorption, biodegradation, hydrolysis and, to a lesser extent, volatilization. The sorption of a given organic compound can be predicted based on its octanol-water partition coefficient, the percent organic carbon in the soil, and the grain-size distribution of the soil.

Determining the relative mobility of contaminants can be helpful in selecting appropriate sampling locations. For example, if wastes containing metals were present in an impoundment, samples to determine the extent of any downgradient metal contamination would normally be collected within a short distance of the impoundment. On the other hand, for fairly mobile waste constituents such as trichloroethylene (TCE), samples could be taken over a much larger downgradient distance. The case study presented below illustrates how contaminant mobility can be estimated.

Facility Description

A 17-acre toxic waste dump was operated in a mountain canyon for 16 years. The facility received over 32 million gallons of spent acids and caustics in liquid

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form. These wastes were placed in evaporation ponds. Other wastes sent to the facility included solvents and wastes from electroplating operations containing chromium, lead, mercury and zinc. Pesticides including DDT had been disposed of in one corner of the site.

Site Description

The site was underlain by alluvium and granitic bedrock (Figure 15-24). The bedrock, as it was later discovered, was fractured to depths of between 50 and 100 feet. Ground water occurred in the alluvial deposits at depths of 10 to 30 feet. Several springs existed in the upgradient portion of the site. A barrier dam was built across part of the canyon at the downgradient edge of the site in an effort to control leakage. Because of the extensive fracture system, this barrier was not effective. Instead, it appears to have brought the ground-water table up into the wastes and, at the same time, pressurized the underlying fracture system, thereby creating seepage of contaminated water under the dam.

Estimation of Contaminant Mobility

Because of the variety of constituents accepted at this site, an estimate of their relative mobility was needed prior to designing the remedial investigation. The first step was to estimate the average linear velocity using the following equation:

$$\bar{v} = \frac{Ki}{n_e}$$

where

$\bar{v}$ = horizontal seepage velocity, ft/day
K = hydraulic conductivity, ft/day
i = ground-water gradient
n_e = effective porosity, decimal fraction.

The hydrogeologic data needed were obtained from existing site assessment reports. The alluvium underlying the site had an average hydraulic conductivity of 0.8 ft/day and an estimated effective porosity of 11 percent. The average ground-

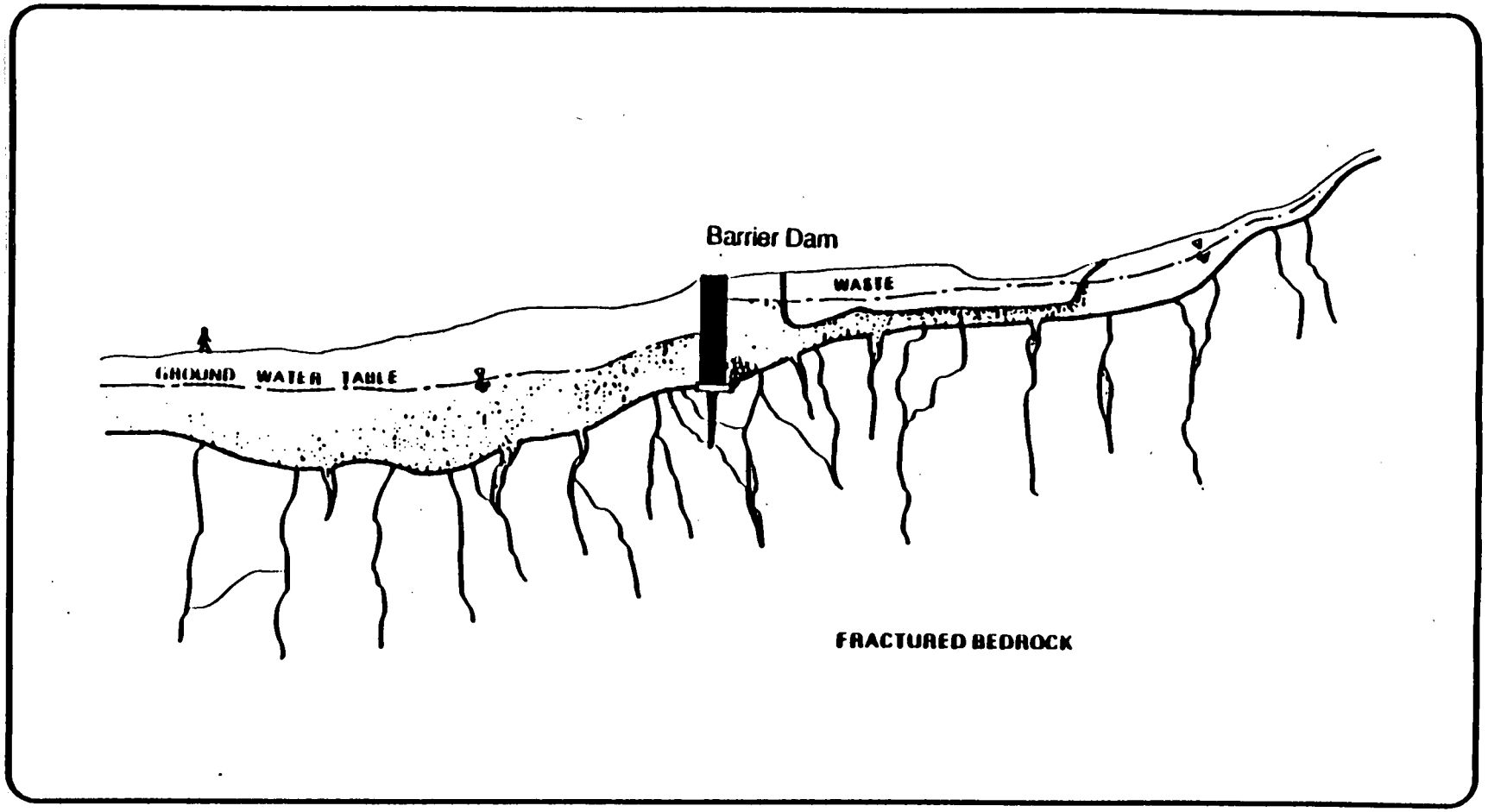

Figure 15-24. Schematic Cross-Section of Waste Disposal Site

water gradient below the site was 0.06. Using the above equation, the average linear velocity was estimated to be 160 ft/yr. This represents the average velocity at which a conservative constituent would migrate downgradient along the centerline of the plume. Examples of such constituents include chloride and bromide. As shown in Table 15-10, nitrate and sulfate also behave conservatively in many cases. Due to the absence of highly weathered, sesquioxide soils, sulfate behaved conservatively at this site. Using the above average linear velocity, an estimate was made of the distance a conservative solute would travel in a given time (T) using $d = \nu T$. Limited water quality data were available for 1980. Wastes were first disposed at this site in 1956. The average extent of plume migration along the centerline was thus estimated to be 3800 feet.

With respect to metals, additional data were needed to estimate their fate including soil pH, presence of carbonates, organic ligands, and percent soil organic matter and clay. At this site, the soil pH varied from less than 3.0 within 400 feet of the acid ponds to 7.2 at a distance 2000 feet downgradient. As shown in Figure 15-25, the partition coefficients for metals are dependent on pH and organic matter content. For example, below a pH of 5.6, for the types of soil encountered at the site, the partition coefficient (Kp) for cadmium is about 10 ml/g. At a pH of 7.2, Kp is about 6500 ml/g (Rai and Zachara, 1985). The relative mobility of attentuated constituents can be estimated as follows (Mills et al., 1985):

$$V_A = \nu / R_d$$

where

V_A = average velocity of attentuated consitutent along centerline of plume, ft/day

ν = average linear velocity as defined above, ft/day

R_d = retardation factor (unitless)

and

$$R_d = 1 + \frac{K_p \rho B}{\eta_e}$$

TABLE 15-10

RELATIVE MOBILITY OF SOLUTES

Group	Examples	Exceptions	Master Variables*
Conservative	TDS		ν
	CL^-		
	BR^-		
	NO_3^-	Reducing conditions	
	SO_4^{2-}	Reducing conditions and in highly weathered soils coated with sesquioxides	
Slightly Attenuated	B	Strongly acidic systems	ν, pH, organic matter
	TCE	Anaerobic conditions	ν, organic matter
Moderately Attenuated	Se		ν, pH, Fe hydroxides
	As		ν, pH, Fe hydroxides
	Benzene		ν, organic matter
More Strongly Attenuated	Pb		ν, pH, SO_4^{2-}
	Hg		ν, pH, C1
	Penta-chlorophenol		ν, organic matter

* Variables which strongly influence the fate of the indicated solute groups. Based on data from Mills et al., 1985 and Roi and Zachara, 1984.

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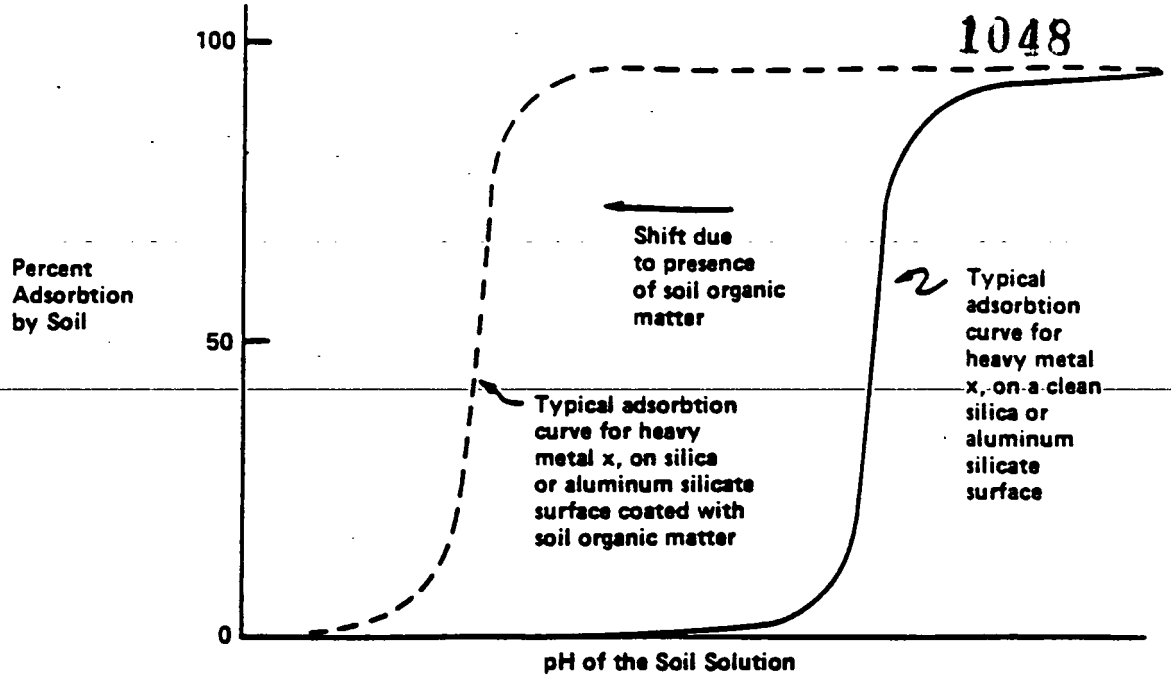
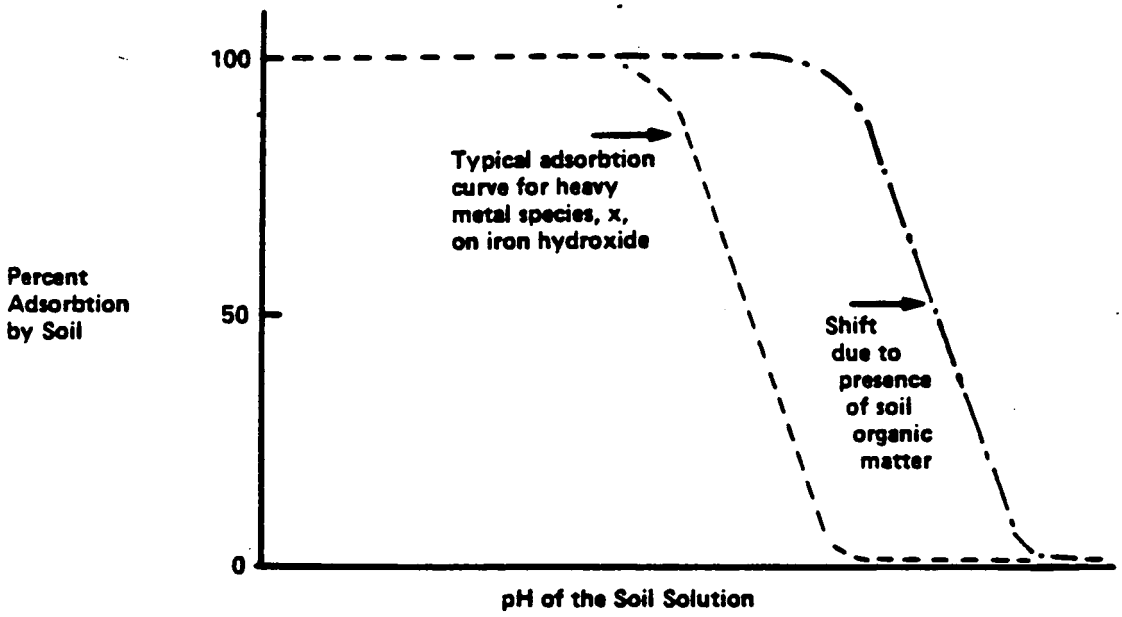


a) Generalized Heavy Metal Adsorbtion Curve for Cationic Species (e.g., $CuOH^+$)



b) Generalized Heavy Metal Adsorbtion Curve for Aniotic Species (e.g., CrO_4^{2-})

Source: (Mills et al., 1985).

Figure 15-25. Hypothetical Adsorption Curves for a) Cations and b) Anions Showing Effect of pH and Organic Matter

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where

K_p = soil-water partition coefficient for solute of concern, ml/g
ρB = soil bulk density, g/ml
η_e = effective soil porosity (decimal fraction).

For example, the relative mobility of cadmium at a pH of 7.2 was estimated for this site as shown below:

$$R_d = 1 + \frac{6500(1.7)}{0.11} = 100{,}456$$

$$V_A = 160/100{,}000 = 0.002 \text{ ft/yr.}$$

This estimate was consistent with the field data which indicated that the metals migrated only until the pH of the contaminant plume was neutralized, a distance of about 2000 feet. Cadmium concentrations decreased from 1.3 mg/l at a distance of 1400 feet from the ponds to below detection (<0.1 µg/l) at a distance of 2000 feet.

Estimates of mobility for organic contaminants which sorb onto soil particles can be made in an analogous manner. The partition coefficient for organic constitutents can be calculated using the following equation (Mills et al., 1985):

$$K_p = K_{oc}[0.2(1-f)X^s_{oc} + fX^f_{oc}]$$

where

K_p = soil-water partition coefficient, ml/g
K_{oc} = organic carbon partition coefficient, ml/g
and
K_{oc} = $0.63\ K_{ow}$
K_{ow} = octanol-water partition coefficient
f = $\frac{\text{mass of silt and clay}}{\text{mass of silt, clay and sand}}$ $(0 \leq f \leq 1)$
X^s_{oc} = organic fraction of sand ($X^s_{oc} \leq 0.01$)
X^f_{oc} = organic fraction of silt-clay ($0 \leq X^f_{oc} \leq 0.1$).

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For example, the solvent trichloroethylene (TCE) has a K_{ow} value of 200. Using the above equation and site data ($f = 0.1$, $X^s_{oc} = 0.001$, $X^f_{oc} = 0.01$), the partition coefficient K_p was estimated to be 0.2 ml/g. The relative mobility of TCE at the site was then estimated to be approximately 40 ft/yr ($R_d = 4$ and $V_A = 40$ ft/yr). Methods for considering additional processes influencing the fate of organics (e.g., hydrolysis and biodegradation) are presented in the manual entitled Water Quality Assessment: A Screening Procedure for Toxic and Conventional Pollutants in Surface and Ground Water (Mills et al., 1985).

Case Discussion

As shown in Figure 15-26, contaminants downgradient of a waste disposal site may migrate at different speeds. Using the methods illustrated above, estimates of the relative mobility of constituents can be made. Such estimates can then be used to locate downgradient monitoring wells and to assist in the interpretation of field data.

References

Mills, W.B., D.B. Porcella, M.J. Ungs, S.A. Gherini, K.V. Summers, L. Mok, G.L. Rupp, and G.L. Bowie. 1985. Water Quality Assessment: A Screening Procedure for Toxic and Conventional Pollutants in Surface and Ground Water. EPA/600/6-85/002a, Vol. I, II and III.

Rai, D. and J.M. Zachara. 1984. Chemical Attenuation Studies: Data Development and Use. Presented at Second Technology Transfer Seminar: Solute Migration in Ground Water at Utility Waste disposal Sites. Held in Denver, Colorado, October 24-25, 1985. 63 pp.

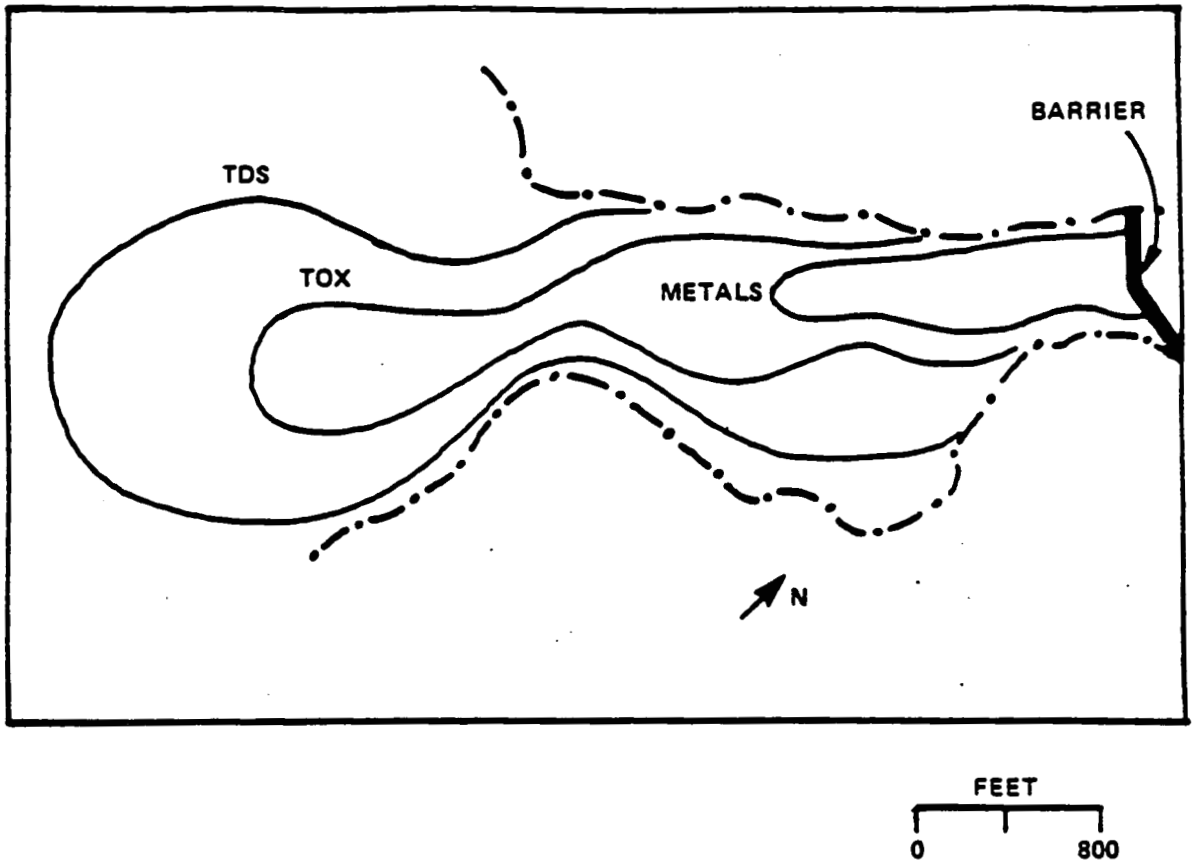

Figure 15-26. Schematic Diagram Showing Plumes of Total Dissolved Solids (TDS), Total Organic Halogens (TOX) and Heavy Metals Downgradient of Waste Disposal Site

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CASE STUDY 16: USE OF LEACHING TESTS TO PREDICT POTENTIAL IMPACTS OF CONTAMINATED SOIL ON GROUND WATER

Point Illustrated

- Soil leaching tests can be used in conjunction with waste and site-specific factors to predict potential impacts on ground water.

Introduction

Contaminated soil, whether deep, or surficial in nature, has the potential to impact ground water, primarily through leaching. In many cases, soil contamination has already lead to contamination of the ground water and decisions can be made regarding clean-up of the contaminated soil and ground water based on the constituent concentrations observed in these media. However, in cases where contaminated soil has not yet resulted in contaminated ground water, but has some potential to do so, decisions need to be made regarding the contaminated soil and whether it should be removed or some other action should be taken because of the soil's potential to contaminate ground water above levels of concern. This evaluation may be especially critical in those cases where only deep soils are contaminated, or where constituent concentrations within surficial soils do not exceed soil ingestion criteria. Both theoretical (mathematical) and physical (leaching test) models can be used in this evaluation, as well as or in conjunction with a qualitative evaluation of release and site-specific factors. This case illustrates the use of leaching tests and consideration of release and site-specific factors to determine whether contaminated soil has the potential to contaminate ground water above levels of concern.

Facility Description

The facility is an industrial chemical and solvent facility located on a leased 2.5 acre site within the corporate limits of a major city in the north-central United States (see Figure 15-27). Periodic overtopping of the surface impoundment, which is now empty, and suspected contamination of the soil with organic solvents from the surface impoundment, resulted in an RFI in which the facility was directed to characterize the nature, extent and rate of release migration.

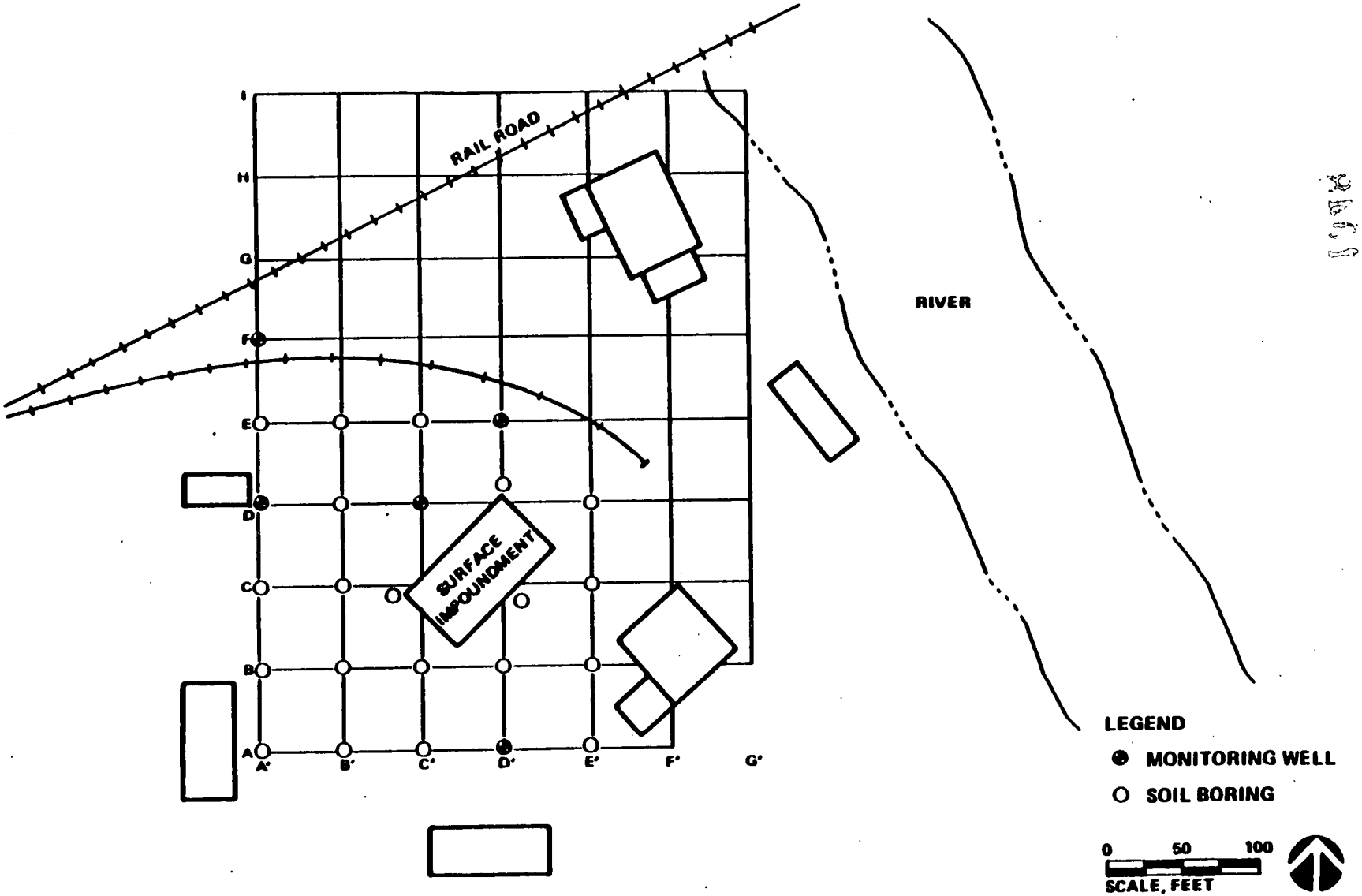

Figure 15-27. Facility Map Showing Soil Boring And Well Installation

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Release characterization revealed that the soil surrounding the surface impoundment, which was mostly fine sand and silt with some clay, was contaminated with tetrachloroethylene and 1,1,1-trichloroethane at concentrations ranging from 0.05 to 0.10 and 2 to 20 mg/kg, respectively. This contamination was observed at depths of up to 5 feet, which was approximately 20 feet above the water table (i.e., the water table was approximately 25 feet below the land surface). The soil beneath the site was relatively permeable, with a hydraulic conductivity of approximately 9×10^{-4} cm/sec.

Ground-water monitoring conducted during the RFI showed no current contamination of the ground water, which flows in a northerly direction and eventually intersects the river (Figure 15-28). The river is used for irrigation and drinking at downstream locations. Grab samples taken from the river and river sediments showed no contamination.

The soil in the immediate vicinity of the railroad spur also showed isolated pockets of mercury contamination, ranging in concentration from 1 to 2 mg/kg, and to a depth of 1 foot below the land surface. The source of the mercury contamination could not be determined.

Contamination Evaluation

The relevant health and environmental (HEA) criteria, the constituent concentrations observed at the site, and selected physical/chemical properties for the three constituents are shown in Table 15-11. Although comparison of the HEA criteria for ingestion with the consituent concentrations observed at the site showed no exceedances, the regulatory agency overseeing the RFI was concerned that leaching of the contaminated soil could lead to eventual contamination of the underlying ground water. This concern was based on the relatively high permeability of the soils beneath the site and the relatively high mobility of the two organic constituents detected. The facility obtained the regulatory agency's approval to conduct a leaching evaluation using EPA's Method 1312 (Synthetic Acid Precipitation Leach Test for Soils).

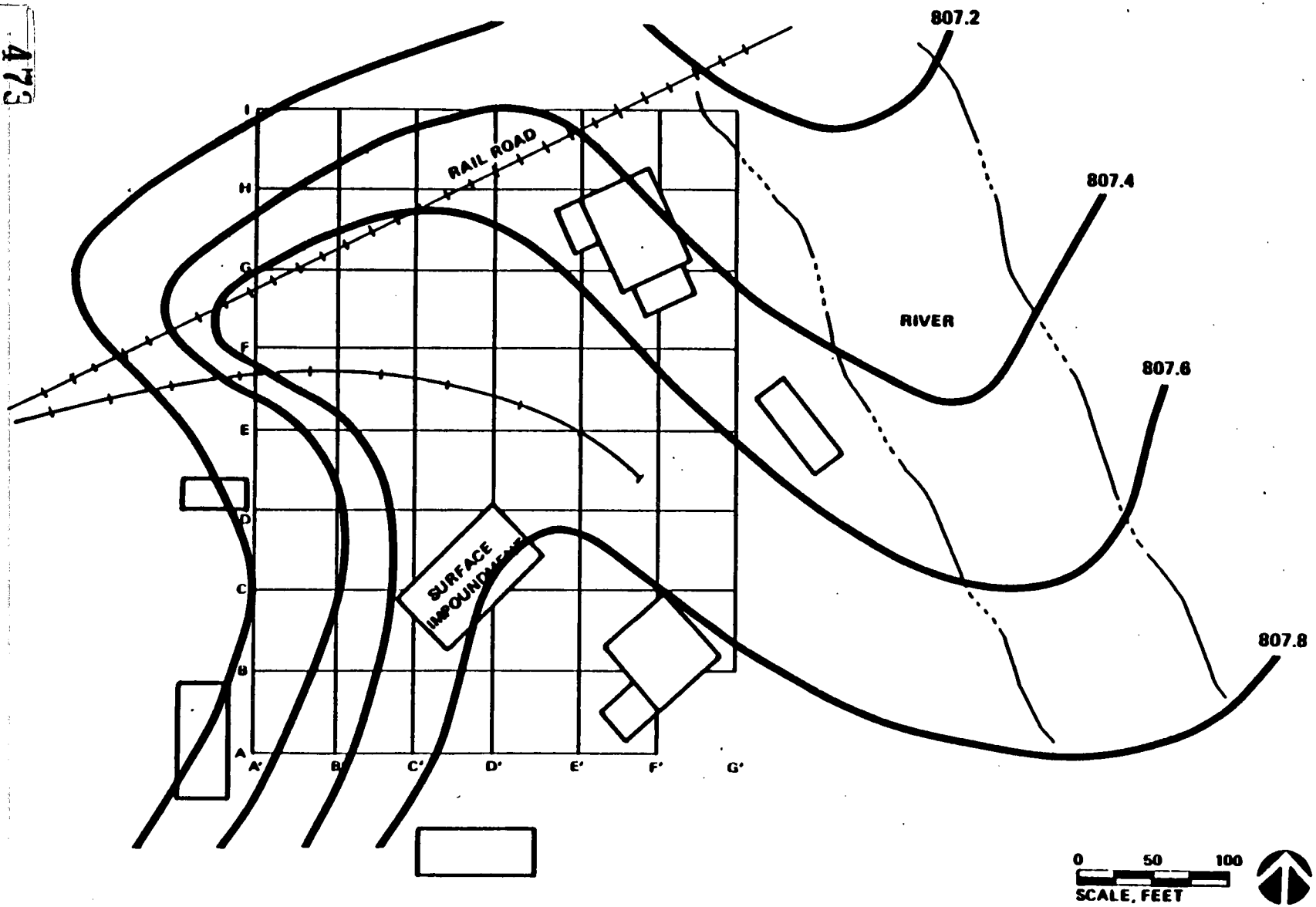

Figure 15-28. Facility Map Showing Ground-Water Contours

TABLE 15-11

HEA CRITERIA, CONSTITUENT CONCENTRATIONS AND RELEVANT PHYSICAL/CHEMICAL PROPERTY DATA FOR CONSTITUENTS OBSERVED AT SITE

Chemical	CAS No.	HEA Criteria (Ingestion) (mg/kg)	H_2O Sol (mg/l)	HEA Criteria (Water) (mg/l)	Constit. Conc. (mg/kg)	Koc (mg/l)	Log Kow	Det. Limit* (mg/l)
Tetrachloroethylene	127-18-4	69	150	0.0069	0.10	364	2.6	0.01
1,1,1-Trichloroethane	71-55-6	2,000	1500	0.2	20	152	25	0.01
Mercury	7439-97-6	--	--	0.002	2	Low	--	0.0004

* Detection limits presented are those for water. Detection limits for soil vary greatly, but may be assumed to be approximately 1 mg/kg.

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Leaching Evaluation

Prior to collecting samples and applying the leaching test, the facility first decided to determine if the contaminated soils could possibly result in leaching test (extract) concentrations that exceed the relevant HEA criteria (See Table 15-11). To do this, the facility calculated the maximum theoretical extract concentration by assuming that 100 percent of the constituents would leach from the soil. The following equation was used:

$$\text{Maximum Theoretical Extract Concentration (mg/l)} = \frac{\text{Concentration of Toxicant in Soil (mg/kg)}}{20}$$

where 20 refers to the liquid to solid ratio applied in EPA Method 1312.

Using this simple equation, the facility determined that the maximum leachate concentration for tetrachloroethylene was, in fact, below the HEA criteria for water (see Table 15-11), and that the level could not possibly be exceeded even if 100 percent of the contaminant leached from the waste. For 1,1,1-trichloroethane and mercury, however, it was determined that the HEA criteria level could be reached if only a portion of the contaminant present leached from the soil, and that application of the leaching test would be necessary. Using this screening-type evaluation, the facility was able to reduce the number of constituents that would need to be analyzed when applying the leaching test, from three to two.

Samples of the contaminated soil were then collected at selected locations (i.e., those expected to produce the more heavily contaminated samples) and Method 1312 applied. Total constituent analyses were also conducted in order to ensure that the samples represented the more heavily contaminated areas of the site. Analyses of the soils and leaching test extract were conducted for 1,1,1-trichloroethane and mercury. The results are shown in Table 15-12.

The leaching test results for 1,1,1-trichloroethane and mercury showed extract concentrations above the respective HEA criteria (action levels) for these

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TABLE 15-12

LEACHING TEST RESULTS (mg/l)*

Constituent	D-C'	C-C'	C-B'
1,1,1-Trichloroethane	0.3	0.2	0.5
Mercury	0.002	0.002	0.003

- Resampled at locations close to original sampling point. Samples analyzed are result of composite of three grab-samples. All samples were taken from the top 0-1 ft of the soil surface.

constituents, indicating that there might be a basis to require some sort of corrective action. The facility, however, presented arguments to show that mercury would be attenuated in the soil column as the leachate percolates towards the water table, and that 1,1,1-trichloroethane would be degraded to below the level of concern in the ground water. Below is a synopsis of the two arguments.

Mercury: The facility first examined theoretical Eh-pH fields of stability for the various aqueous mercury species; determined that the predominant mercury species would be elemental mercury, and further predicted (using Eh-pH diagrams) that the maximum equilibrium concentration of elemental mercury in water would be 0.025 mg/l. The facility interpreted the substantially lower leaching test concentration to indicate that attenuation processes such as sorption play a major role in restricting the mobility of elemental mercury. The facility cited high soil/water partition coefficients (i.e., Kd values), and several scientific studies to further support their contention that mercury would strongly sorb to both organic and inorganic components of the soil before any leachate reached the ground water.

1,1,1-Trichloroethane: The facility recognized that due to its high solubility (1500 mg/l) and low Kd (0.011 ml/g), 1,1,1-trichloroethane would not be attenuated appreciably as the leachate percolates towards the water table. The facility argued, however, that abiotic hydrolysis would significantly degrade 1,1,1-trichloroethane during leaching. Several environmental half-life studies were cited which indicated that the half life for 1,1,1-trichloroethane ranged between 0.5 and 2.5 years. Based on these studies, the facility predicted that 1,1,1-trichloroethane would be degraded to below levels of concern within one to three years. Using additional site information and simple time of travel calculations, the facility predicted that concentration levels for 1,1,1-trichloroethane would be decreased to below the level of concern well before reaching any potential receptors.

The regulatory agency's evaluation of the facility's arguments is presented below:

Mercury: The facility's argument with respect to mercury is essentially correct if it can be assumed or proven that the mercury originally present at the site is inorganic in nature. If, however, the mercury present is organic in nature (e.g.,

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methyl mercury), the potential for migration of the mercury is substantially increased. Organic mercury compounds generally have higher volatility, higher solubility, and much lower Kd values than inorganic mercury compounds. It should also be noted that even if the original release was of inorganic mercury, biotransformation (i.e., biomethylation) of elemental mercury may occur. The facility should be required to determine the actual form(s) of mercury present at the site.

1,1,1-Trichloroethane: The facility's argument with respect to 1,1,1-trichloroethane raises many technical questions. For example, the facility uses published data on the half life of 1,1,1-trichloroethane, which may not be applicable to the facility's soil and ground-water environment. As another example, the half-life degradation rate argument may only be applicable for ground-water transport. The facility does not address degradation in soil or effects on surface water (assuming that contaminated ground-water will eventually migrate to the river). Most important, however, is the fact that the facility did not address the degradation products of 1,1,1-trichloroethane, one of which is 1,1-dichloroethylene, which is also a hazardous constituent. 1,1,1-trichloroethane should be assumed to pose a threat to ground water.

Conclusions

The next step in the RFI process would be to determine if interim corrective measures or a Corrective Measure Study was warranted for the release. Although none of the soil ingestion HEA criteria were exceeded at the site, application of the leaching evaluation indicated that 1,1,1-trichloroethane could leach to ground water and result in exceedance of the HEA criterion for water. On this basis, the facility should be directed to perform a Corrective Measures Study.

To prevent further contaminant migration, the application of interim corrective measures may also be considered. Construction of a temporary cap over the contaminated area is one option. Perhaps a more appropriate measure would be to remove the contaminated soil. Such an action, taken as an interim corrective measure, may negate the need for a formal Corrective Measures Study.

Case Discussion

Leaching tests and similar evaluations (e.g., application of validated mathematical leaching models) can be used to identify potential problems due to leaching of contaminated soils. In this case, application of a leaching evaluation was instrumental in identifying a potential threat to ground water as a result of leaching of contaminated soil. This finding was particularly significant as HEA ingestion criteria were not exceeded.

It should be noted, however, that in some cases leaching tests may provide results that are difficult to interpret. For example, consider what would have happened if the soil underlying the facility was predominantly clay with a permeability on the order of 10^{-8} cm/sec. In this case, demonstrating that leaching will most likely occur within the forseeable future may be difficult. As another example, if the soil underlying the facility were predominantly sand, leaching would be probable. In both these cases, application of a leaching test may not provide any more useful information than is already available. Careful consideration of release and site-specific information is always warranted prior to application of leaching tests.

CASE STUDY 17: USE OF SPLIT-SPOON SAMPLING AND ON-SITE VAPOR ANALYSIS TO SELECT SOIL SAMPLES AND SCREENED INTERVALS FOR MONITORING WELLS

Point Illustrated

- HNU and OVA/GC screening can provide a relative measure of contamination by volatile organics. It can be used to select soil sample locations and can assist in the selection of screened intervals for monitoring wells.

Introduction

On-site vapor screening of soil samples during drilling can provide indications of organic contamination. This information can then be used to identify apparent hot spots and to select soil samples for detailed chemical analyses. In this manner, the use of higher powered laboratory methods can be focused in an effective way on the analysis of samples from critical locations and depths. The vapor analyses on site can also be helpful in selecting screened intervals for monitoring wells.

Facility Description and History

Manufacturing of plastics and numerous other chemicals has occurred at the site over the past 30 years. Some of the major products included cellulose nitrate, polyvinyl acetate, phenol, formaldehyde, and polyvinyl chloride. The entire site covers 1,000 acres. The location of the buildings and waste disposal areas are shown in Figure 15-29. This is the same facility as used in Case Studies 7, 8 and 14.

Three disposal methods are known to have been employed at the site. Readily combustible materials were incinerated in four burning pits, while non-combustibles were either disposed of in landfills or in a liquid disposal area. All on-site disposal operations were terminated in 1970, and monitoring programs have been implemented to identify contaminants, define and monitor ground-water contaminant plumes, and assess the resulting environmental impacts.

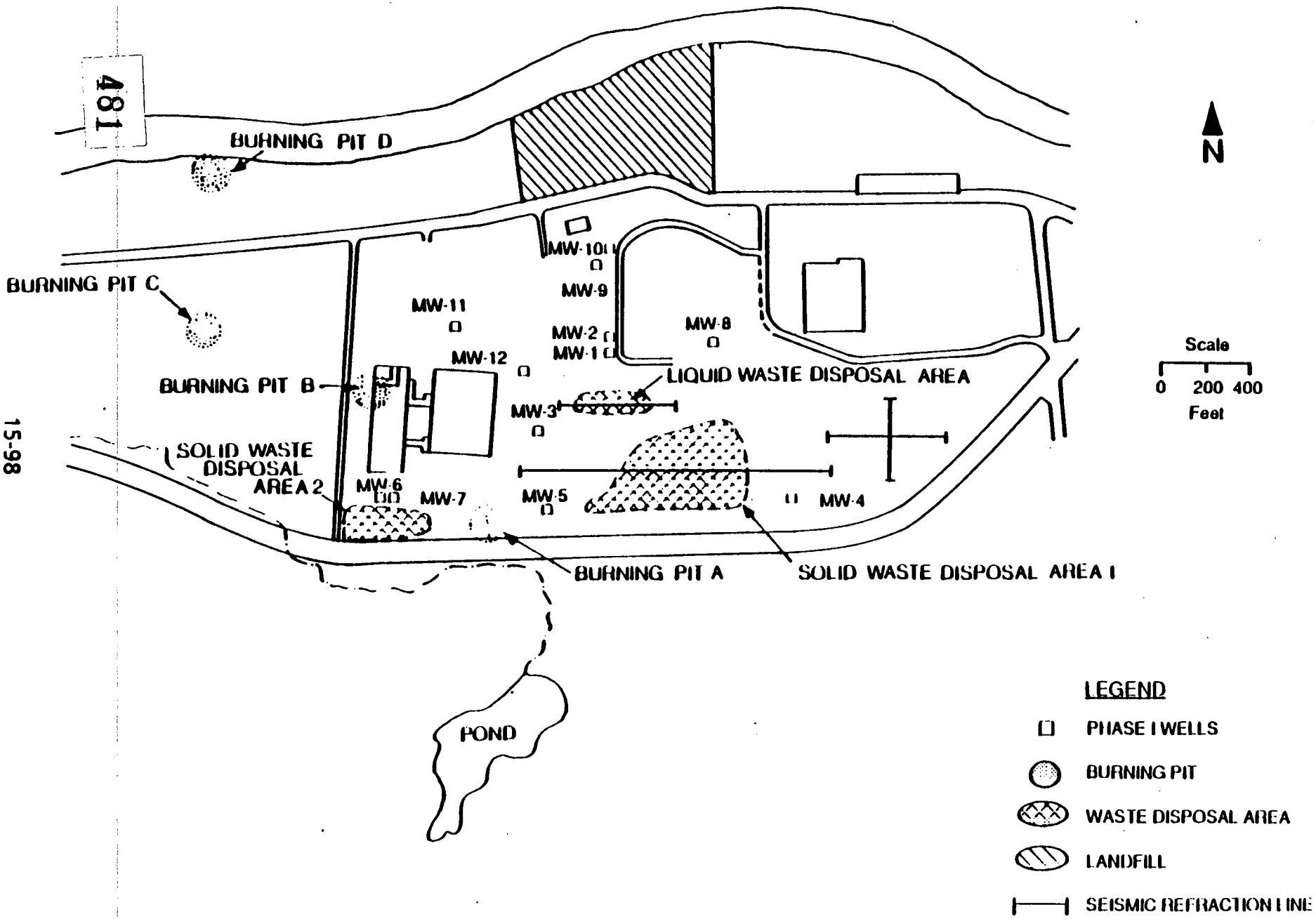

Figure 15-29. Site Plan Showing Disposal Areas and Phase I Well Locations

Geologic and Hydrologic Setting

The site is located in a well-defined glacial valley, adjacent to a river. Three major units underlie the site, consisting primarily of sand and gravel outwash deposits; fine-grained lacustrine sands; and till. The middle sand unit contains lenses of silt, clay and till. Only the deep till formation appears to be continuous across the site. A geologic cross-section beneath two of the disposal areas is shown in Figure 15-30.

The ground-water flow direction at the site is to the northwest. However, there appears to be a buried stream channel running across the site which strongly influences the local ground-water flow regime (see Figure 15-31). Ground water from the site is thought to discharge to the river. The depth to ground water varies from 10 to 40 feet.

Sampling Program

As part of the remedial investigation at this site, 33 borings were drilled using a hollow-stem auger rig. Continuous soil samples were collected using split-spoon samplers. Samples for laboratory chemical analysis were selected based on the volatile organic concentrations detected by initial vapor screening of the soil samples in the field.

This field screening was achieved by placing a portion of each sample core in a 40 ml glass headspace vial. An aliquot of gas was extracted from the vial and injected directly into a portable OVA gas chromatograph (OVA/GC). The chromatograph was equipped with a flame ionization detector to identify hydrocarbons. Each sample was also screened using an HNU photoionization detector because of its sensitivity to aromatic hydrocarbons, particularly benzene, toluene and the xylenes. Following completion of drilling, gamma logs were run on all boreholes.

An example of the vapor screening results (HNU and OVA/GC) and geological and gamma logs for one of the boreholes are shown in Figure 15-32. The data shown demonstrate the differential sensitivity of the HNU and OVA/GC detectors. Because the OVA/GC is more sensitive to the organics of interest (aliphatics),

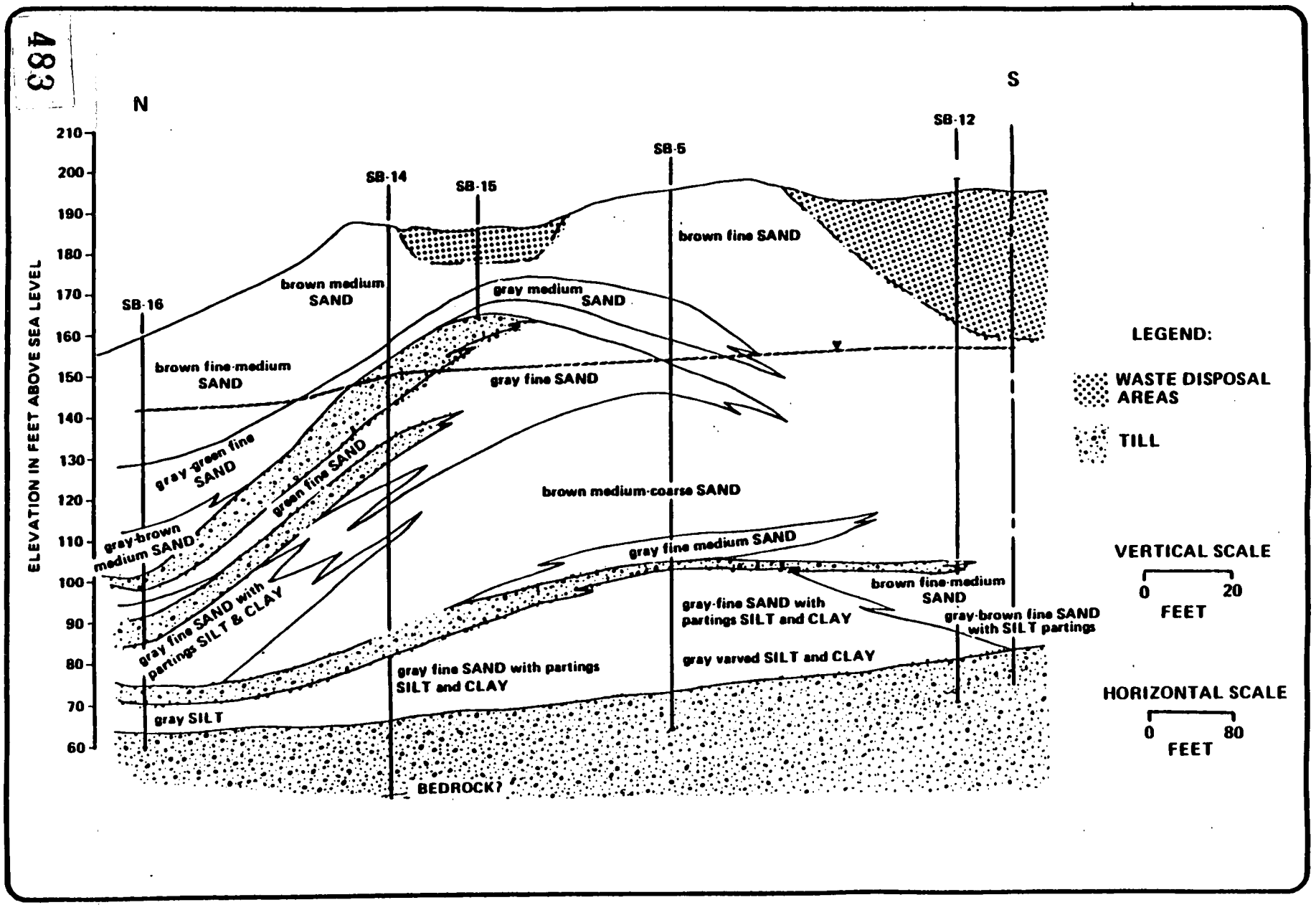

Figure 15-30. Geologic Cross-Section Beneath Portion of Site

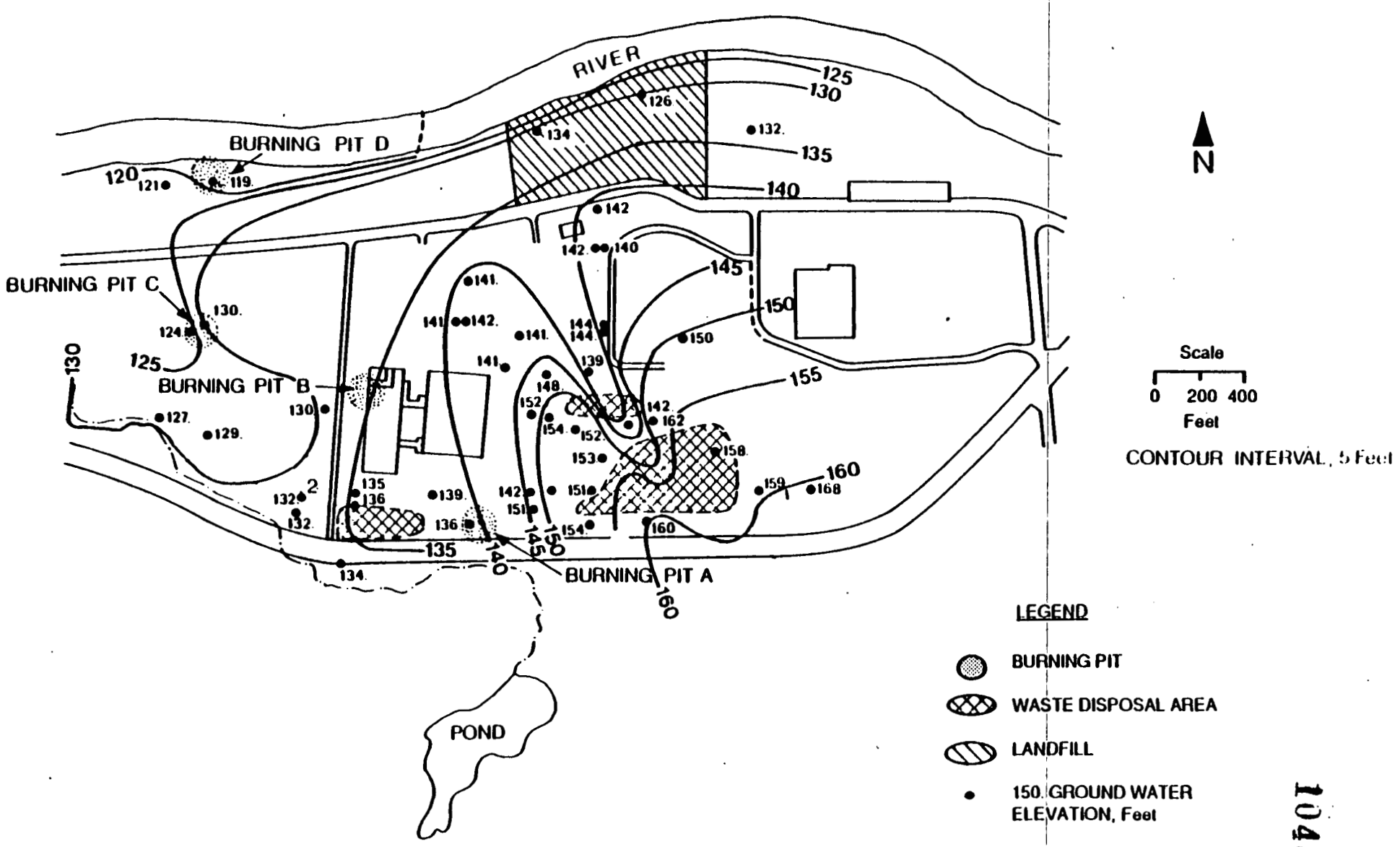

Figure 15-31. Ground-Water Elevations in November 1984

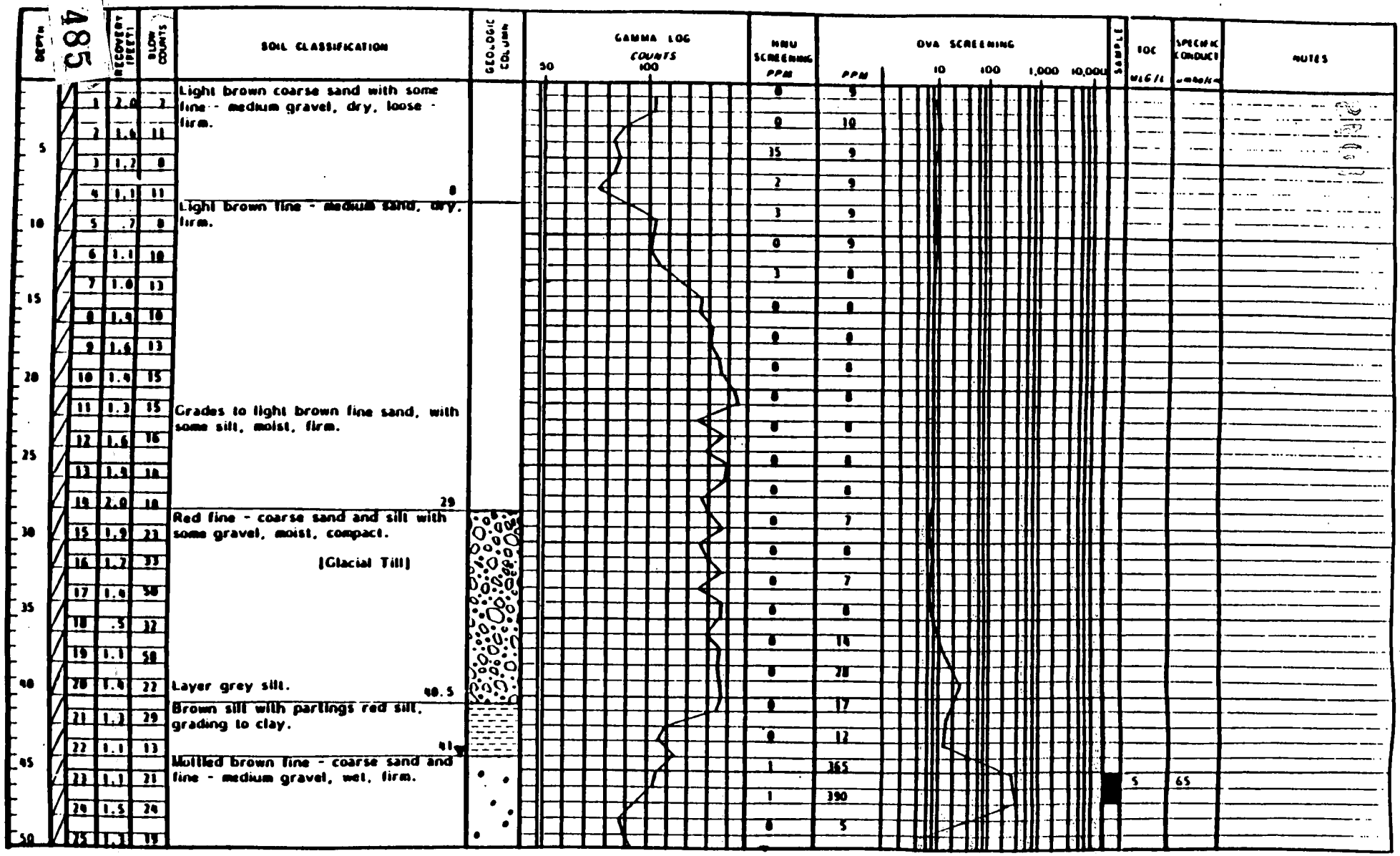

Figure 15-32. Example of Borehole Data Including HNU and OVA/GC Screening

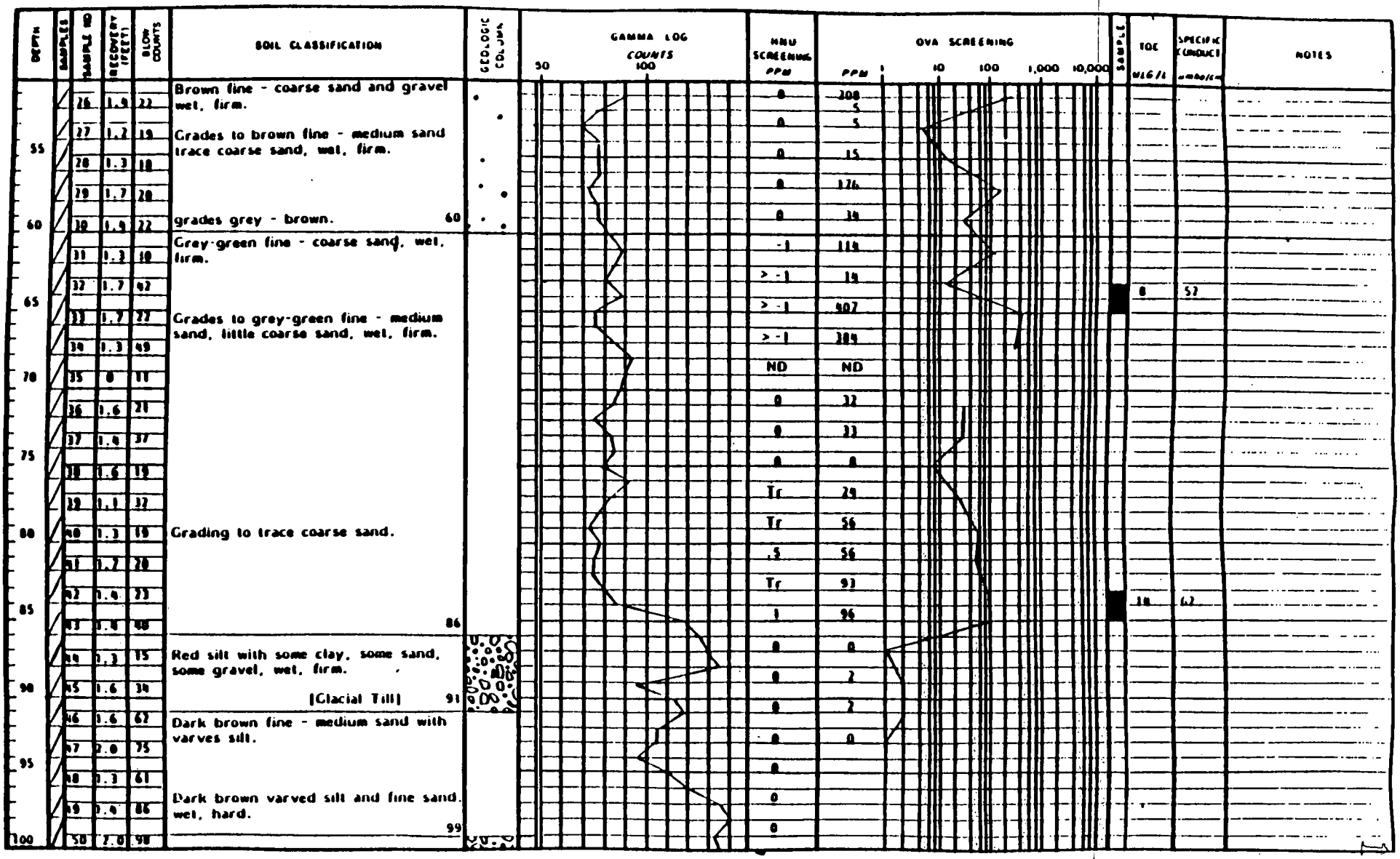

Figure 15-32. Example of Borehole Data Including HNU and OVA/GC Screening (continued)

these results were used to select samples for detailed chemical analysis in the laboratory. As shown in Figure 15-32, samples in zones with OVA/GC readings of 365 ppm (45 feet deep), 407 ppm (65 feet deep), and 96 ppm (85 feet deep) were selected. In the laboratory, samples were first analyzed for total organic carbon (TOC). The ten samples with the highest TOC levels were then analyzed for purgeable organics using EPA Method 50-30 and extractable organics using EPA Method 82-50 (U.S. EPA, 1982 - Test Methods for Evaluating Solid Waste, SW 846).

The OVA/GC results were also used to select well screen intervals. Examination of the data in Figure 15-32 shows that the highest levels of volatile organics (by OVA/GC) were found at a depth of 65 feet. In addition, the gamma and geologic logs indicated that the permeable medium at that depth was coarse sand which would be a suitable location for the placement of a well screen. Thus, a 5-foot stainless steel screen was set over the depth interval of 62 to 67 feet.

Case Discussion

This sampling program incorporated field techniques that detect the presence of volatile organics and allow on-site, rapid identification of likely contaminant "hot spots" for detailed laboratory anaysis and to select depths for monitoring well screens.

CASE STUDY 18: CONDUCTING A PHASED SITE INVESTIGATION

Points Illustrated

- When ground-water contamination is known or suspected at a site, a set of initial borings is typically made to determine site hydrogeologic characteristics and to identify areas of soil and ground-water contamination (Phase I).

- These findings are then used to select well locations to fully delineate the extent of contamination (Phase II).

Introduction

To identify the extent of ground-water contamination in an efficient manner, information is needed on the ground-water flow regime. Phase I investigations typically focus on determining site geologic characteristics and ground-water flow directions and velocities. Waste sources are also identified. The Phase I results are then used in planning the Phase II investigation to determine the extent of contamination and to refine estimated rates of contaminant migration.

Facility and Site Description

Descriptions of the facility and site geologic characteristics were included in Case Studies 7, 8, 14 and 17.

Sampling Program

The Phase I sampling program included geophysical surveys, water level monitoring, soil sampling, and ground-water quality sampling. Three seismic refraction lines were run to estimate the depth to the top of the deep till. The top of the till was found to occur at a depth of 70 to 120 feet over most of the site.

Available historical data indicated that the general ground-water flow direction was to the northwest across the site. The ground water was thought to discharge to the river. This information and historical drawings and maps of known

disposal areas were used to locate the Phase I borings (see Figure 15-29 in Case Study 17). One well (MW4) was located on the suspected upgradient side of the site. The other wells were located near waste sources to determine which sources appeared to be contributing contaminants to the ground water. For example, two wells (MW6 and 7) were immediately downgradient of solid waste disposal area #2. To determine the presence of vertical gradients, three two-well clusters were drilled--each with one well screened just below the water table and a second well screened considerably below that at the base of the till.

The results of the Phase I investigation indicated that all the wells contained solvents. Thus, investigations of the waste sources and contaminant plumes were continued in Phase II. The highest solvent concentrations were found in wells located near the liquid waste disposal area where downward vertical gradients were present. The contaminants had migrated down to depths of 75 feet in this portion of the site. The Phase I data confirmed the general northwest ground-water flow direction but showed a complex flow pattern near the buried stream channel. A second concern was whether observed lenses of fine-grained till under the site were producing localized saturated zones which could be contaminated.

Based on the Phase I results, a Phase II monitoring program was designed to determine the extent of contamination around the major disposal sites. Typically, two soil borings were made - one up- and one downgradient of the waste source. Because of the high solvent concentrations observed in the wells downgradient of the liquid disposal area, a more intensive field investigation of this area was included in Phase II. Instead of two borings per waste source at the liquid disposal area, 11 soil borings and five new monitoring wells were drilled. This represented one-third of the total effort for the entire 1,000 acre site. The total number of Phase II soil borings was 33 (Figure 15-33) and the total number of Phase II wells was 15 (Figure 15-34). The Phase II data indicated that most of the solvent contamination originated from the liquid disposal area and not from solid waste disposal area #1 which is upgradient of the liquid disposal area. The Phase II data did identify PCBs from solid waste disposal area #1 but not from any of the other sources. This was consistent with site records indicating that transformers had been disposed at this area.

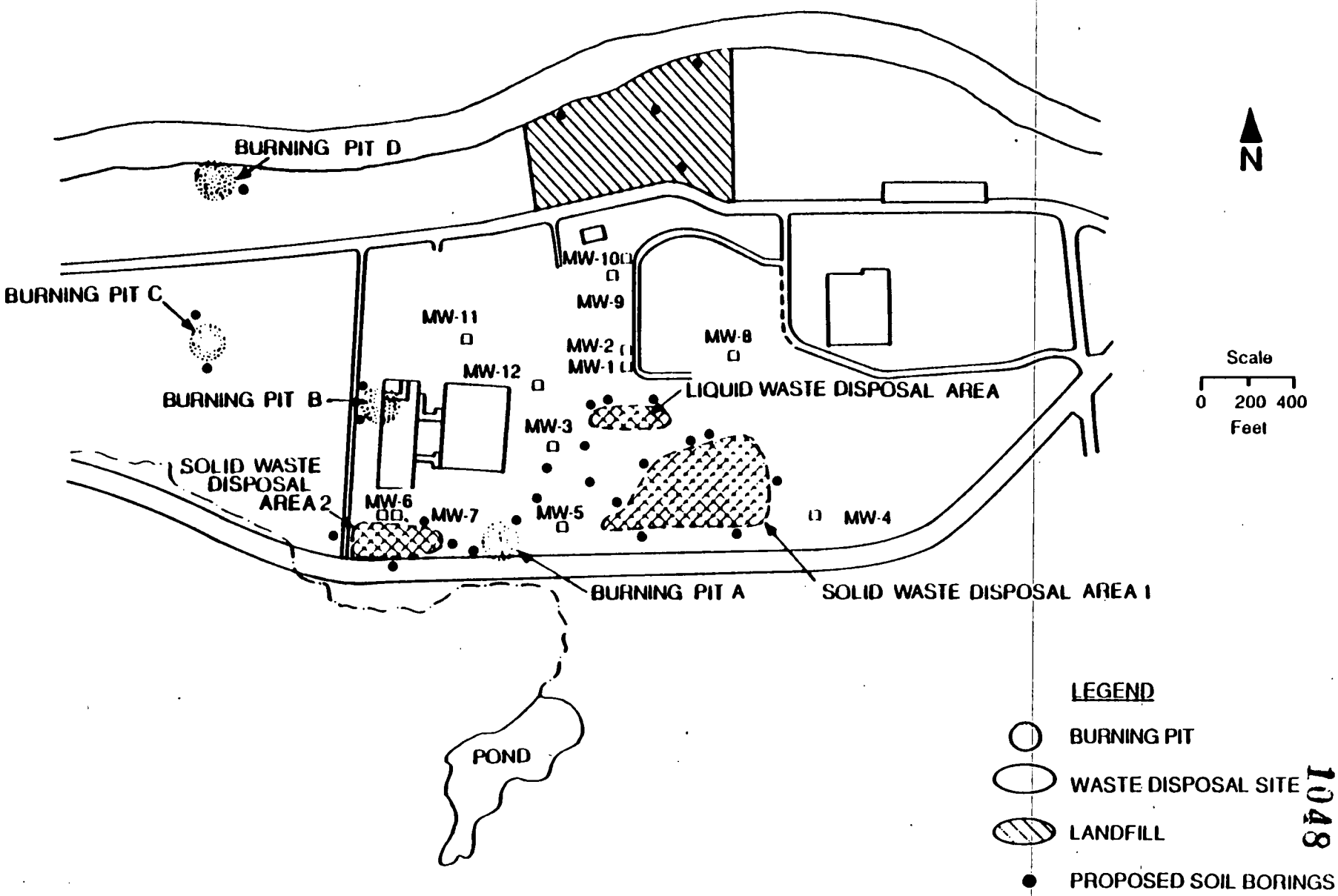

Figure 15-33. Proposed Phase II Soil Borings

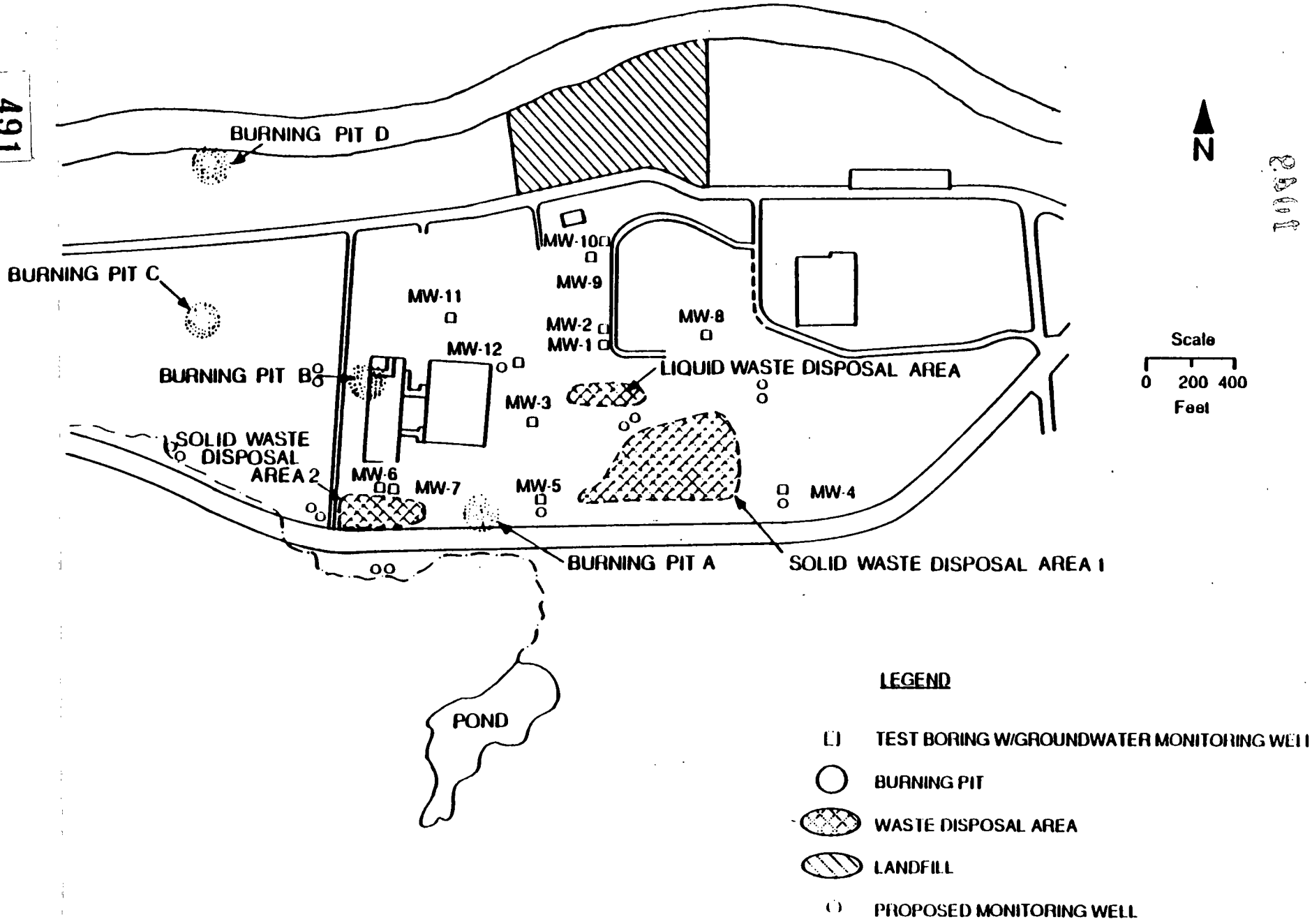

Figure 15-34. Proposed Phase II Monitoring Wells

Case Discussion

Investigation of a large complex site is commonly conducted sequentially. Basic information is needed on site geologic characteristics and ground-water velocities and directions to appropriately locate wells for determining the extent of contamination. Thus, the initial installation of a limited number of exploratory borings and wells can provide the data needed to design a complete and effective investigation. Results from the latter investigation can then be used to determine the need for remedial action and to evaluate alternative remediation methods.

CASE STUDY 19: MONITORING BASEMENT SEEPAGE

Point Illustrated

- Basement monitoring can be used to estimate the extent of contaminant migration.

Introduction

Leachate produced in a landfill can be transported downgradient in ground water by advection and dispersion. Shallow ground water may surface and seep into basements.

Site Description

A channel, originally constructed as part of a hydroelectric power generation system, was used as a disposal site for a variety of chemical wastes from the 1920s through the 1950s. More than 21,000 tons of waste were dumped in and around the site before its closure in 1952. After closure, homes and a school were constructed on and around the site. In the 1960s, residents began complaining of odors and residues. During the 1970s, the local water table rose, and contaminated ground water seeped into nearby basements.

Geologic and Hydrologic Setting

Figure 15-35 shows a cross-section of the site. The site has both a shallow and a deep aquifer. The shallow aquifer consists of approximately 5 feet of interbedded layers of silt and fine sands overlying beds of clay and glacial till. The deeper aquifer is a fractured dolomite bedrock overlying a relatively impermeable shale. Travel times from the shallow to the deeper aquifer are relatively long. Contamination has occurred in the shallow aquifer because of the "bathtub effect". The impermeable channel filled because of infiltration, and leachate spilled over the channel sides. The leachate contaminated the shallow ground water and was transported laterally in this system.

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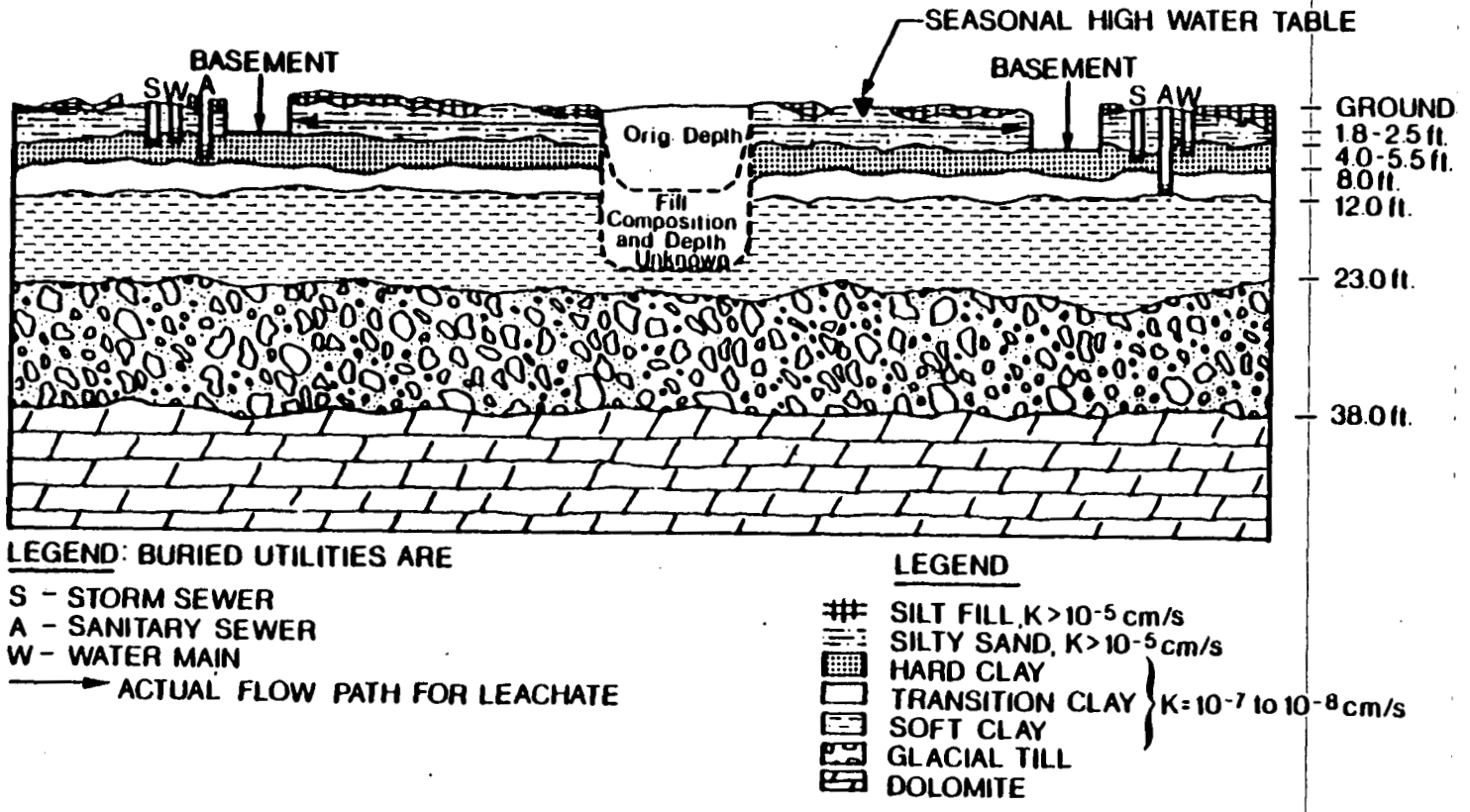

Figure 15-35. Geologic Cross-Section Beneath Site

Sampling Program

The houses surrounding the channel were grouped into three sets (upgradient, downgradient, and on-site) based on preliminary data on the underlying strata and ground-water flow directions. Four houses from each group were selected for sampling for a total of 12 houses. Samples of water and sediments were collected from the sump pump wells in each basement. Water samples were collected when the sump pumps were running and 24 hours after pumping had ceased. Water and sediment samples were analyzed for purgeable and extractable organics. Benzene, carbon tetrachloride, chloroform, and trichloroethylene (TCE) were found in the water samples. Water samples taken while the sump pumps were running had higher concentrations of volatile organics. Sediment samples contained PCBs and dioxin, possibly due to cosolvation. Relatively immobile organics can become dissolved in another more mobile solvent. The mobile solvent containing traces of other organics can be advected along with the water. This process (cosolvation) is one facet of enhanced transport which has recently been proposed as a possible mechanism for the observed mobility of otherwise immobile organics. Samples of water and sediments from storm drains were also collected and analyzed to determine if discharges from the sumps to the storm drains were a significant source of organics in the storm runoff.

In addition to determining water quality, indoor and outdoor air quality was measured in the basements at each house. Tenax and polyurethane foam tubes were placed in air monitoring systems in each basement to measure 12-hour average concentrations of volatile organics (e.g., carbon tetrachloride, benzene, and TCE) and semi-volatile organics (e.g., pesticides). Volatile organics were present in the indoor air samples but semi-volatile organics were not detected. The highest volatile organic concentrations were observed when the sump pumps were operating.

Case Discussion

At sites where hydrogeologic factors favor shallow lateral ground-water flow, initial site characterization may involve sampling of basements. Results from such an initial site characterization can provide information on contaminant migration

which can be used in the design and implementation of detailed soil and ground water monitoring programs.

The results of the sampling program described above led to the evacuation and destruction of a number of homes. A system of monitoring wells has been installed to replace the basement sump sampling sites. The shallow aquifer is being pumped and treated to arrest contaminant migration.

CASE STUDY 20: USE OF PREDICTIVE MODELS TO SELECT LOCATIONS FOR GROUND-WATER MONITORING WELLS

Point Illustrated

- Simple mathematical models can be used to estimate the longitudinal and transverse spread of a contaminant plume. Wells can then be located in areas expected to have elevated contaminant concentrations and in areas thought to be both up- and downgradient of the plume.

Introduction

The use of mathematical models to estimate the migration of contaminants can be helpful for several reasons, including: 1) fewer wells may be needed to delineate a contaminant plume, and 2) wells can be rationally located in an attempt to determine the maximum concentrations in a plume, its furthest extent, and locations where concentrations should be at background levels.

Facility Description

The site was an electronics manufacturing plant that had been in operation for 20 years. Four large diameter, rock-filled "dry wells" had been used to dispose of solvents and process wastes. These disposal units were between 35 and 60 feet deep. Depth to ground water was over 460 feet. Disposal Units 1 and 2 had received paint wastes and solvents, including trichloroethylene (TCE) and tetrachloroethylene, between 1964 and 1979. Disposal Units 3 and 4 had been used to dispose of plating solutions and spent acids between 1971 and 1977. These solutions contained copper, chromium, nickel, lead and tin. All the disposal units were closed in 1982. Exact quantities of wastes disposed are not known.

Geologic and Hydrologic Setting

The site is located in a large alluvial basin in an arid region. The basin alluvium is over 1,000 feet thick and consists of an upper sand and gravel unit, a middle silty-clay unit, and a lower sand and gravel unit. Granitic bedrock underlies the unconsolidated formations. Prior to large withdrawals of ground water, the upper

unit had been saturated. At present, the silty-clay unit acts as an aquitard so that water beneath it is under confined conditions. The potentiometric surface is now 350 feet below the land surface. In addition to a drop in water level elevations, the ground-water flow direction has changed over the years from east to north in response to changing pumping regimes. Estimated horizontal flow velocities have varied from 10 to 40 feet/year.

Site Investigation

In 1982, city water officials discovered TCE in water samples from wells within 3 miles of the site. On its own initiative, the site owner began a pre-remedial investigation, and then later a remedial investigation, to determine whether his site could be a source of the TCE. The pre-remedial investigation provides an example of how simple models can be used to determine well locations. The pre-remedial investigation included sampling nearby wells and drilling a single deep sampling well (over 500 feet deep).

Original plans called for locating the deep monitoring well between the waste disposal units in an attempt to determine whether solutes had contaminated the underlying ground water. However, site constraints, including an overhead power transmission line, underground power lines and major manufacturing buildings, necessitated that the monitoring well site be moved. The next step was to determine an appropriate location for this well. Because of the changing ground-water flow direction at this site, it was decided to use a simple mathematical model to predict the areal extent of contamination from the disposal units. The results would then be used in selecting a new location for the deep monitoring well. Data were collected to determine historical hydraulic gradients, pumping histories, and aquifer hydraulic characteristics (e.g., conductivity, porosity). Following data collection, a vector analysis model "the method of Mido" (1981) was used to predict plume evolution. The results showed that the major plume migration was to the north (Figure 15-36). Thus, the well was located north of the disposal units at a distance of 60 feet from Unit 4.

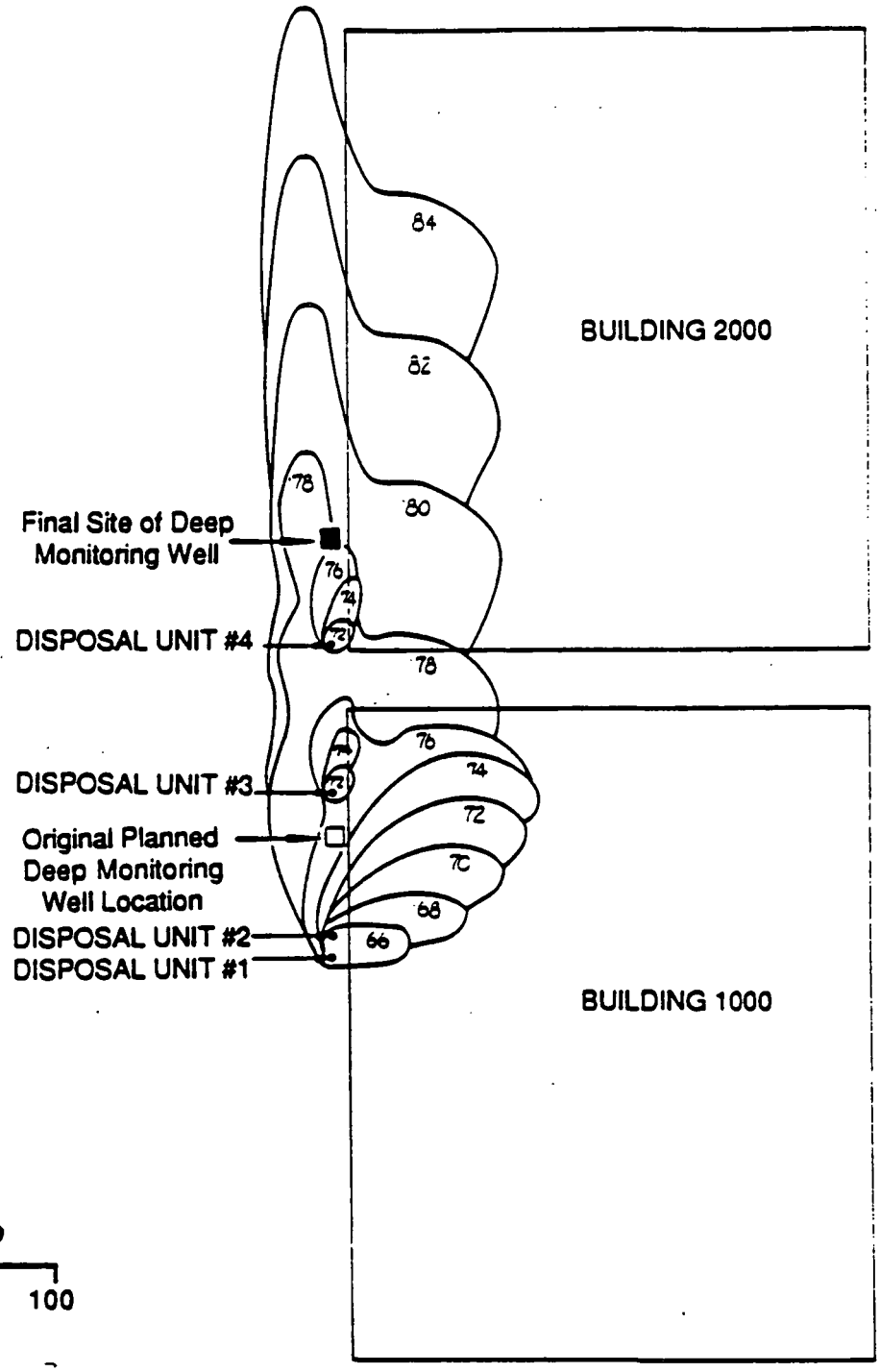

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Figure 15-36. Estimated Areal Extent of Hypothetical Plumes from Four Wells

Case Discussion

Use of a model to predict potential plume migration at this site provided a means of evaluating the long-term consequences of changing ground-water flow directions and velocities. Thus, the pre-remedial investigation deep monitoring well could be sited in the direction of net plume displacement, rather than at a location which might have had a low probability of intercepting contaminated ground water. A concentration below the detection limits from a well located beyond the expected plume boundaries would have been inconclusive (for example, see Figure 15-37). However, the deep monitoring well was located close to the disposal units and in the direction of plume migration. Additional wells are now being planned for the full-scale remedial investigation.

Reference

Mido, K.W. 1981. An economical approach to determining extent of ground water contamination and formulating a contaminant removal plan. Ground Water, Vol. 19, No. 1, pp. 41-47.

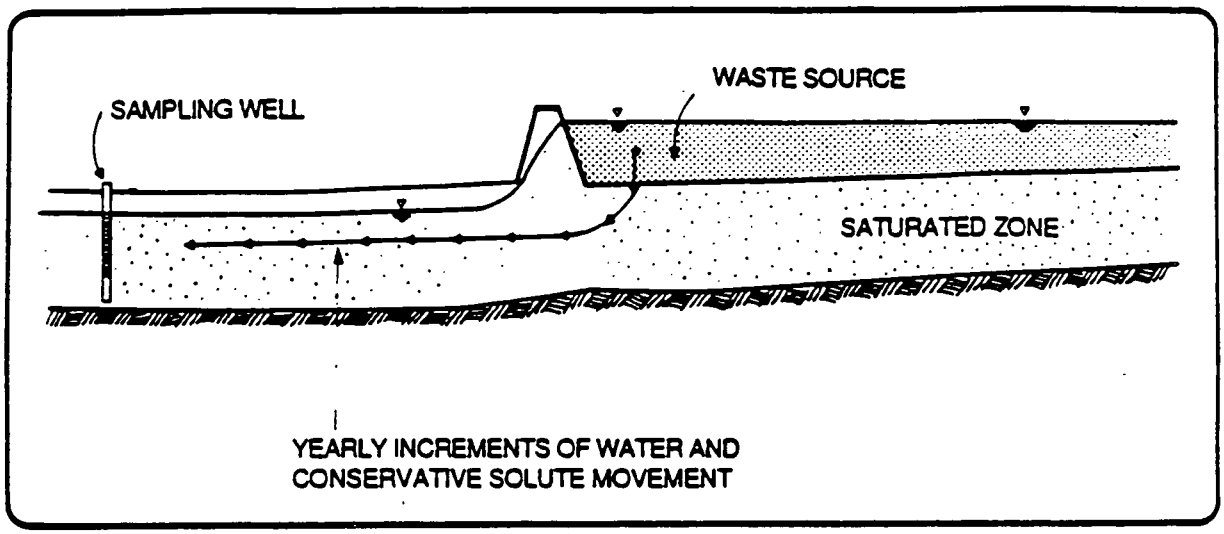

Figure 15-37. Consideration of Solute Migration Rates in Siting Sampling Wells.

If a monitoring well is sited farther downgradient than solutes could have traveled in the time since disposal, low concentrations in the well would certainly not prove that ground-water contamination had not or was not occurring. Prior to locating a well, average linear velocities should be estimated ($v = Ki/n_e$ where v = average linear velocity for conservative solutes, K = hydraulic conductivity, i = ground-water gradient, and n_e = effective porosity). Using these estimates, and the age of the disposal unit, T, an approximate migration distance, D, can be computed ($D = T/v$) for conservative solutes associated with the waste. For soil interactive solutes, migration distances will be less. Methods for estimating these distances are given by Mills et at. (1985).

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CASE STUDY 21: MONITORING AND CHARACTERIZING GROUND-WATER CONTAMINATION WHEN TWO LIQUID PHASES ARE PRESENT

Point Illustrated

- Monitoring and characterizing ground-water contamination when two or more liquid phases are present requires knowledge of the physical and chemical properties of each phase.

Introduction

Ground-water supplies are susceptible to contamination by immiscible organic liquids. Organic liquids such as PCB-contaminated transformer oils, petrochemical solvents, and motor fuels, because of their nature, often form a second liquid phase. This separate liquid, in either the vadose or saturated zone, represents a problem in multiphase flow. It is necessary to understand how these separate phases behave when designing monitoring and sampling programs for sites contaminated with such liquids. Techniques commonly used for single-phase flow systems may not be appropriate.

Site Description

The facility is a transformer manufacturing plant which experienced a major discharge of polychlorinated biphenyls (PCBs) and trichlorinated benzenes (TCBs). The discharge resulted from a break in a buried pipeline, but surface spillage may have also occurred during production. The volume and duration of the subsurface discharge is not known; neither is the quantity released by above ground spillage.

Geological and Hydrologic Setting

The site is comprised of 10 feet of fill over lacustrine clay which varies in thickness from 20 to 30 feet. Fractures with openings of approximately 0.1 cm have been observed in the clay. Below the clay lies a thin silt layer. Below that is a 40- to 60-foot-thick layer of glacial till composed of fine sand near the top, and gravel, sand, and silt below.

Perched water about 3 feet deep flows laterally in the fill. The permanent water table, located in the till, is partially confined. Potentiometric levels in this latter system are between 25 and 30 feet below the land surface.

Sampling Program

Over 1000 soil samples were taken as part of the site investigation. A mobile atmospheric pressure chemical ionization mass spectrophotometer (APCI/MS) was employed for rapid, on-site characterization of soil samples. This instrument can detect PCBs down to a minimum concentration of 100 mg/kg. About 20 percent of the PCB analyses were replicated by conventional gas chromatography.

Granular dry materials were sampled from an auger with care taken in cleaning sampling equipment to avoid cross-contamination. In taking samples from the clay, special effort was made to sample the surfaces of obvious fractures. This was done to maximize the changes of detection of PCBs in largely uncontaminated soil. Due to dilution, large bulk samples can prevent the detection of contaminant migration through fractures in low permeability soils.

Vertically, the soil sampling program showed PCBs to be distributed in a non-homogeneous pattern within the clay zone. Concentrations of PCBs greater than 500 mg/kg PCBs were detected. The lateral spreading of PCBs throughout the fill was much more extensive than the vertical movement. This could be due to the nature of the discharge/spillage, pressure from the broken pipe, or the fact that the fill is more permeable than the clay. The PCBs appear to have formed a layer along the fill/clay interface. Movement of PCBs more than 300 feet laterally from the original spill site has been confirmed.

Based on the soil sampling results, 12 well locations (Figure 15-38) were chosen to further characterize the site. Four boreholes were drilled into the till aquifer. One well, 686-B, was placed upgradient of the spill site with a screened interval between depths of 45 and 50 feet. The three downgradient wells in the till aquifer were screened over different intervals to increase the possibility of detecting a separate organic liquid layer. The screened intervals used were at depths 45 to 50 feet (well 686-A), 50 to 55 feet (well 686-C), and 55 to 60 feet (well 686-D). Eight

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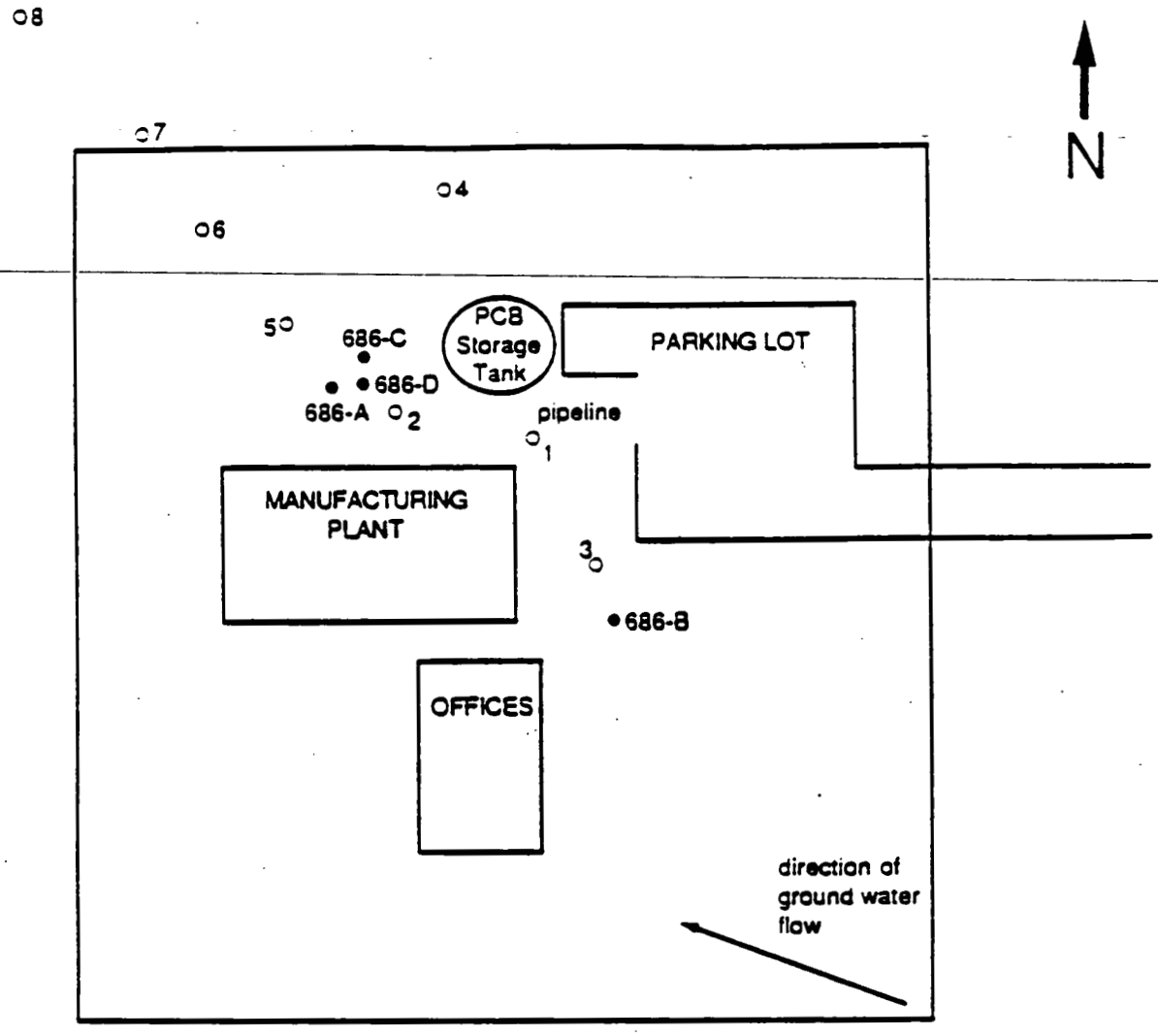

● deep well locations
○ shallow well locations

Figure 15-38. Well Locations and Plant Configuration

shallow wells were also placed in the fill to monitor the perched water. The fill is approximately 10 feet deep and a layer of PCBs was suspected at the fill/clay interface. The depth of the perched water fluctuates between 7 and 8 feet. Six of the eight wells in the fill, 1, 3, 4, 6, 7, and 8, are screened from 7 to 10 feet. Samples from wells 1, 6, 4, and 7 showed PCB levels much higher than the solubility limits. The sampling results suggest that two separate liquid layers exist at these locations and that the liquids are being mixed during sampling. Wells 2 and 5 were screened from 5 to 8 feet to determine if a floating liquid layer was present. Again, samples having concentrations far in excess of solubility limits indicated the existence of a layer of organic liquid.

Case Discussion

Ground-water systems contaminated with immiscible liquids require special attention. Well screen intervals should be placed to intercept flow along boundaries between soil layers of differing hydraulic conductivities and at water table surfaces. Sampling results must also be interpreted properly. Samples showing contaminant concentrations far in excess of solubility limits may indicate that two layers of different liquids are being pumped and mixed.

Finally, Figure 15-39 is offered as an illustration of the types of complexity which can be encountered with immiscible liquids having densities both greater than and less than water.

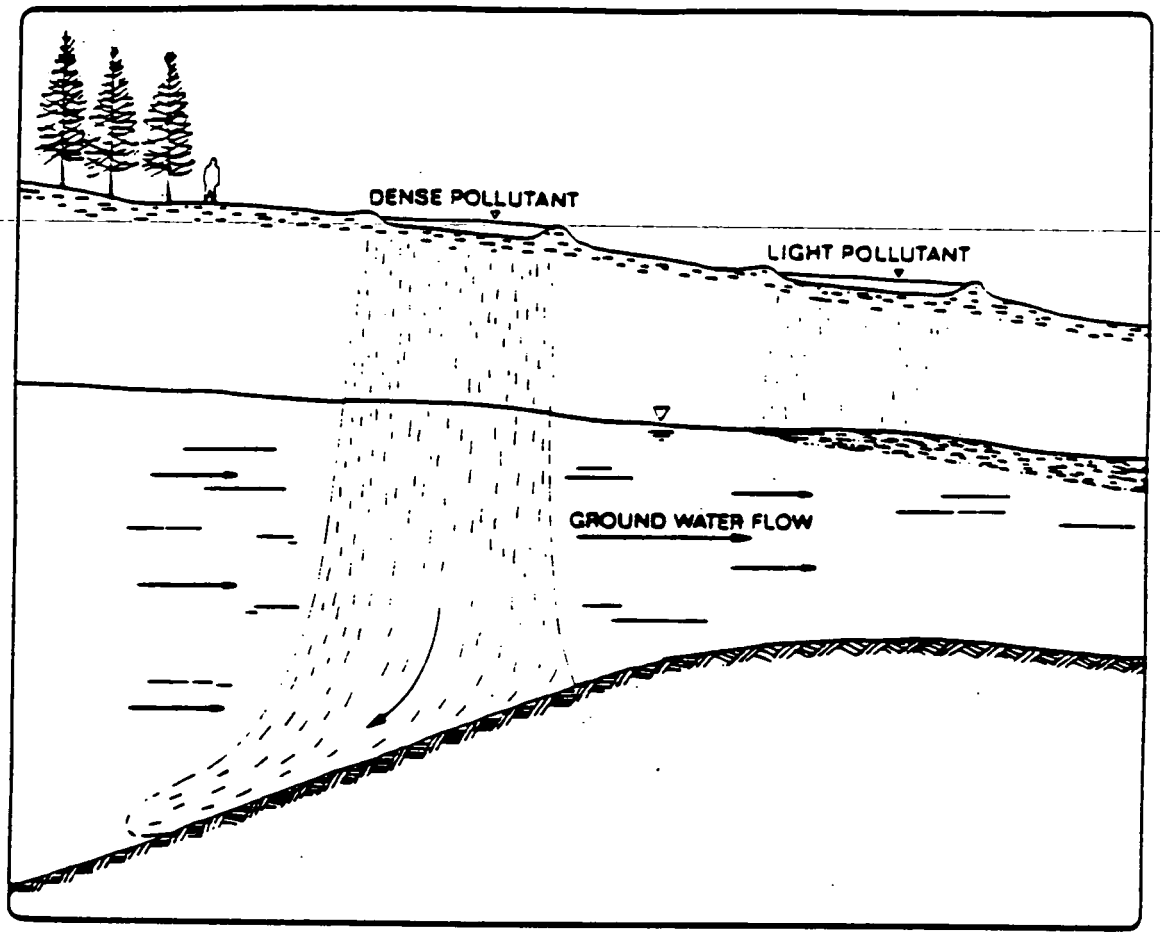

Figure 15-39. Behavior of Immiscible Liquids of Different Densities in a Complex Ground-Water Flow Regime

CASE STUDY 22: METHODOLOGY FOR CONSTRUCTION OF VERTICAL FLOW NETS

Point Illustrated

- Construction of a vertical ground-water flow net can be a valuable tool for evaluating ground-water (and contaminant) pathways and for determining additional actions that may be necessary to accurately delineate the ground-water flow regime at a facility.

Introduction

Constructing a vertical flow net at a facility provides a systematic process for analyzing the accuracy of ground-water elevation and flow data, and can therefore foster a better understanding of the ground-water flow regime at the site.

Facility Description and History

The site contains a large chemical manufacturing facility of approximatley 300 acres located beside a major river in the northeastern United States. The site has been used for chemical manufacturing by different companies since 1904 and has a long history of on-site waste management. Several solid waste management units have been identified at the facility. This is the same facility as discussed in Case Studies 7, 8, 14, 17 and 18.

Geologic and Hydrologic Setting: At depths of 150 to 200 feet the site is underlain by bedrock identified as arkosic sandstone. Above this bedrock are glacial deposits consisting of a thick bed of hard till, overlain by lacustrine sediments and deltaic and outwash deposits. Discontinuous lenses of till were identified within the deltaic deposits. A trough cut into the thick-bedded till and trending approximately southeast to northwest has been identified. See Figure 15-40.

The river beside the facility flows westward and discharges into the main stem of a larger river approximately 4 miles west of the facility. A small tributary (brook) borders the facility to the southwest and west. Swamp-like areas are present near

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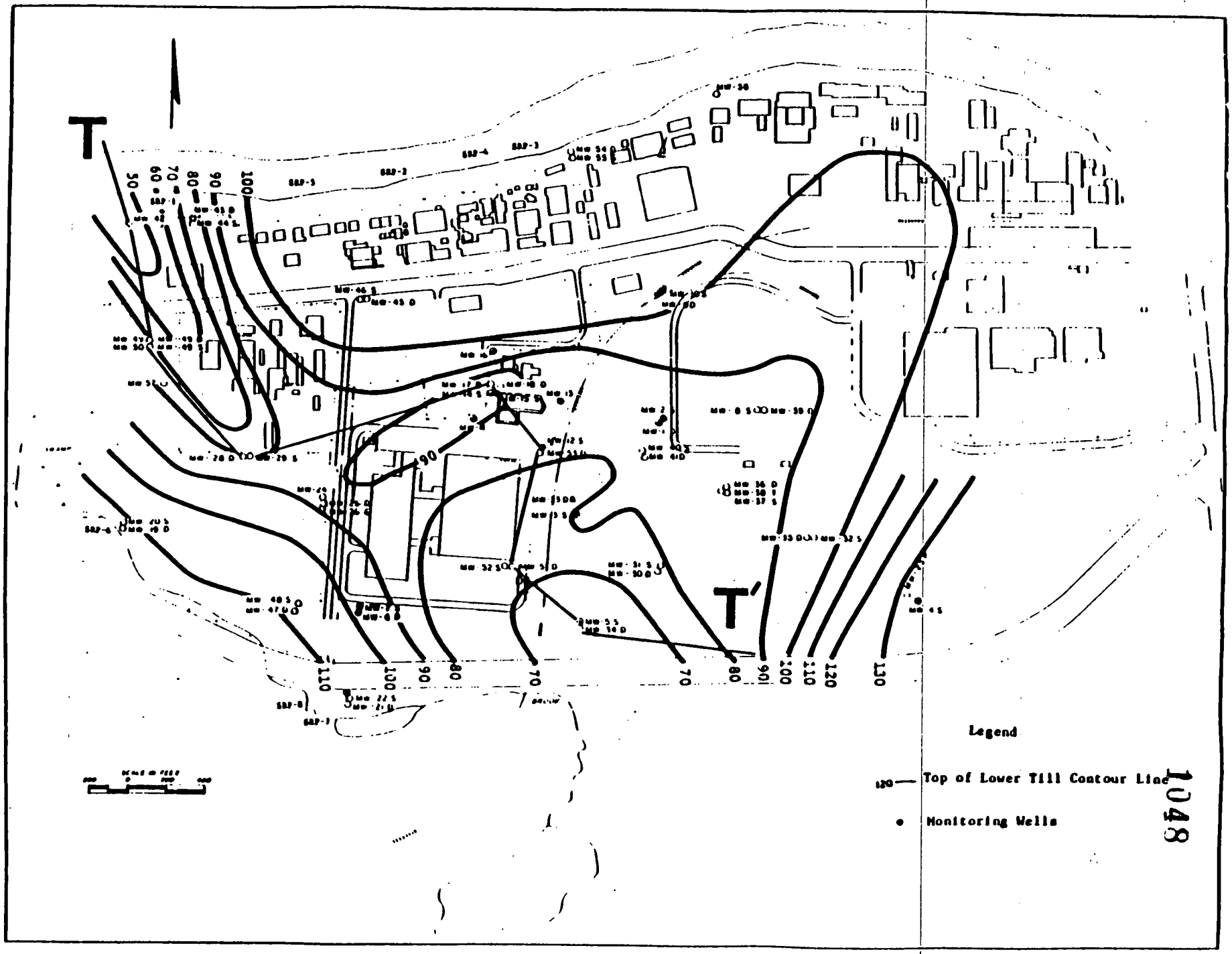

Figure 15-40. Top of Lowest Till Contour Map and Location of Vertical Flow Net

the tributary. It is suspected that the arkosic sandstone outcrops in the river adjacent to the facility. Whether this visible rock is a large glacial erratic or an outcrop of the arkosic sandstone bedrock is an issue identified during previous investigations and may be important in characterizing the ground-water flow regime at the facility.

Program Design

The site was investigated in two phases. Phase I (1981-1984) included the installation and monitoring of wells MW-1 through MW-12, while Phase II (1984-1985) consisted of 34 soil borings, installation of wells MW-13 through MW-57, and monitoring and sampling of all wells. This two-phased approach allowed the use of the initial monitoring well data and soil boring data to determine the placement of the Phase II monitoring wells. Further discussion of this two-phased approach is provided in Case Studies 7 and 18.

Data Analysis

Evaluation of the data was conducted based on information provided by the owner or operator, including the water-level elevation data presented in Table 15-13. Well locations and water-level elevations in the wells were mapped and compared to elevations of the midpoint of the well screens to show relative hydraulic head differences from well to well. Vertical gradients are a reflection of different head values at different elevations. For each well, the head can be determined at the elevation of the midpoint of the well screen by measuring the water-level elevation in the well. Different head values corresponding to different screen elevations were used to evaluate vertical gradients. During the plotting of this map, anomalous data were identified and marked for further investigation.

The geology of the site and the depositional processes forming the aquifer were studied to determine what sorts of hydrogeologic phenomena might be expected. Glacial outwash deposits exhibit trends in sediment size and sorting. Sediment size decreases and sorting increases from the marginal to the distal portions of the deltaic/lacustrine deposits.[1] It is expected that this tendency will be

[1]Mary P. Anderson, "Geologic Facies Models: What Can They Tell Us About Heterogeneity," presented to the American Geophysical Union, Baltimore, May 18, 1987.

TABLE 15-13

GROUND-WATER ELEVATION SUMMARY TABLE PHASE II

Well Number	Ground Elevation (ft)	Well Depth (ft)	Midpoint of Well Screen Elevation[1]	Screen Length (ft)	Water Level Elevation 9/1/82
MW-1	162.80	76.50		3	
MW-2	162.50	22.50		3	
MW-3	174.20	31.00	145.7	3	150.54
MW-4	201.90	54.00	150.4	3	156.85
MW-5	186.30	47.50	141.3	3	149.95
MW-6	144.30	39.50	107.3	3	135.78
MW-7	144.60	19.50	127.6	3	135.94
MW-8	155.10	24.00	133.6	3	149.04
MW-9	160.50	61.00	135.0	3	141.53
MW-10	160.40	30.00	132.9	3	144.62
MW-11	154.70	27.00	130.2	3	140.57
MW-12	159.50	26.50	135.5	3	141.05
MW-13	162.20	29.00	139.2	10	141.22
MW-14	162.10	29.00	139.1	10	140.66
MW-15	162.00	29.00	139.1	10	140.67
MW-16	162.00	29.00	135.5	3	140.87
MW-17	162.00	71.00	104.5	25	140.52
MW-18	161.90	72.00	103.4	25	140.53
MW-19	137.10	24.00	116.6	5	127.83
MW-20	137.20	17.00	123.7	5	127.82
MW-21	141.40	26.50	118.4	5	135.39
MW-22	141.60	15.10	13.0	5	135.35
MW-23	204.30	225.50	-10.2	20	184.98
MW-24	143.90	70.00	76.4	5	136.47
MW-25	143.80	39.00	107.3	5	130.20
MW-26	143.80	24.00	123.2	5	130.17
MW-27*					
MW-28	142.70	46.00	100.2	5	127.86
MW-29	142.80	23.00	123.3	5	127.88
MW-30	172.00	85.50	90.0	5	152.70
MW-31	172.20	24.85	150.8	5	151.68
MW-32	203.10	61.00	145.6	5	154.78
MW-33	174.20	94.00	83.7	5	150.49

*Not installed.
[1]Assumes screens are installed one foot above the bottom of the well.

TABLE 15-13 (continued)

Well Number	Ground Elevation (ft)	Well Depth (ft)	Midpoint of Well Screen Elevation[1]	Screen Length (ft)	Water Level Elevation 9/1/82
MW-34	186.20	75.80	113.9	5	149.72
MW-35	203.20	106.25	100.4	5	144.31
MW-36	189.40	101.20	91.7	5	143.22
MW-37	189.50	48.00	145.0	5	150.51
MW-38	189.30	135.30	57.5	5	145.04
MW-39	154.90	68.00	90.5	5	142.45
MW-40	173.80	47.50	129.8	5	146.59
MW-41	173.70	75.30	101.9	5	141.95
MW-42	134.20	64.00	73.7	5	117.62
MW-43	139.50	32.10	80.9	5	117.24
MW-44	139.50	28.00	115.0	5	119.62
MW-45	144.32	35.00	112.8	5	128.97
MW-46	144.15	25.00	122.6	5	126.48
MW-47	141.50	34.00	111.0	5	131.91
MW-48	141.60	17.00	128.1	5	131.74
MW-49	143.00	72.20	74.3	5	123.22
MW-50	143.00	30.20	116.3	5	123.85
MW-51	157.00	70.30	90.2	5	149.58
MW-52	157.00	34.00	126.5	5	139.48
MW-53	159.30	77.90	84.9	5	141.09
MW-54	145.80	52.00	97.3	5	120.18
MW-55	145.90	35.00	114.4	5	121.63
MW-56	133.60	20.30	116.8	5	119.84
MW-57	141.90				
Screen Reference Points					
SRP-1				114.41	
SRP-2				114.92	
SRP-3				116.05	
SRP-4				115.86	
SRP-5				NA	
SRP-6				128.81	
SRP-7				137.28	
SRP-8				134.11	

*Not installed.
[1]Assume screens are installed one foot above the bottom of the well.

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reflected in hydraulic conductivities throughout the outwash deposits at the facility. There is some suggestion of such a trend in the head data from the site.

The map of hydraulic head values and screen midpoint elevations were evaluated considering both the possible hydrogeologic phenomena expected for the geology of the area and the depositional processes creating the aquifer. Several working hypotheses were developed to explain the apparent ground-water flow patterns and the identified vertical gradients.

- Hypothesis 1: Vertical gradients can be explained by classifying areas where the vertical gradients were reflective of discharge and recharge areas. (See Figure 15-41.)

- Hypothesis 2: The top surface of the till forms a trough with a saddle. (See Figure 15-40.) The vertical gradients showing higher head with depth reflect the movement of water as it flows upward over the saddle.

- Hypothesis 3: The vertical gradient may correlate with locations of buildings and parking lots at the site. Recharge occurs primarily where the ground is not paved. The downward gradient near the river may be caused by runoff flowing downhill and recharging the ground water at the edge of the pavement.

- Hypothesis 4: Most of the ground-water flow is horizontal. The vertical gradients reflect phenomena whose scale is smaller than the resolution of available data, and an accurate interpretation cannot be made. Geologic systems exhibit heterogeneity on different scales, causing fluctuations in head on different scales. The small-scale fluctuations detected at the site are due to undefined causes and may represent:

  1. details of stratigraphy (such as till beds in parts of the outwash deposit),
  2. artificial recharge and discharge (such as leaky sewer pipes), or
  3. errors in the data.

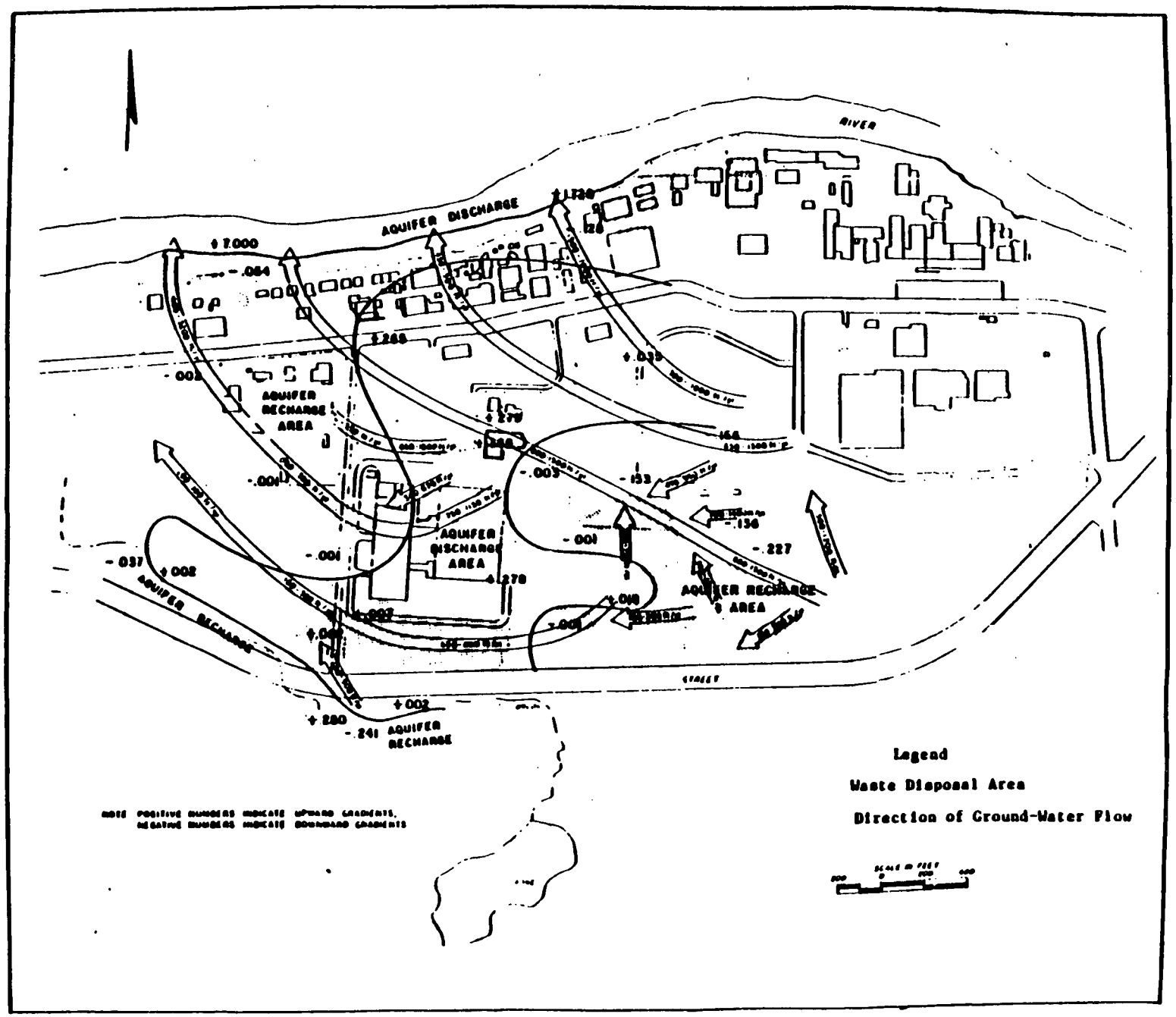

Figure 15-41. Recharge/Discharge Areas and Flow Directions

To characterize flow at the site and to support the design of corrective measures (if needed), a working (conceptual) model of flow at the site should be developed. This model, in this case a vertical flow net, can be used to identify data gaps and to prioritize gathering of the necessary additional information. Considering the hypotheses developed, an area for characterizing the vertical flow regime was selected. Determination of this area, where a geologic cross-section and flow net will be constructed, was based on:

- Assumptions and requirements necessary to construct flow nets, as identified in the Criteria for Identifying Areas of Vulnerable Hydrogeology, Appendix B: Ground-Water Flow Net/Flow Line Construction and Analysis (Vulnerable Hydrogeology, Appendix B). For example, ground-water flow should be roughly parallel to the direction of the cross-section and vertical flow net.

- Flow being representative of the hydrogeology of the facility.

- Flow representing the major paths of ground-water movement. For example, the aquifer is shaped like a trough and a major portion of the ground-water flow occurs in the middle of this trough; therefore, a cross-section and flow net should be constructed along the axis of the trough.

A geologic cross-section was constructed for the area of interest and is identified as T-T' in Figure 15-40. A flow net was then constructed following the methodology described in Vulnerable Hydrogeology, Appendix B; see Figure 15-42. Construction of a vertical flow net requires a graphical solution of Darcy's Law. Data that do not fit the solution become evident in Figure 15-42 as shown, for example, by the head value for MW 52.

Construction of a vertical flow net allowed for a systematic evaluation of the various hypotheses. Hypothesis 1, where vertical gradients are labeled recharge and discharge, is rejected because the gradients vary significantly in a very irregular pattern (compare well clusters MW 14-18 and MW 12 and 53); there is no apparent reason that natural recharge would vary so irregularly. Hypothesis 2 seemed reasonable initially but, after closer inspection, is rejected because upward

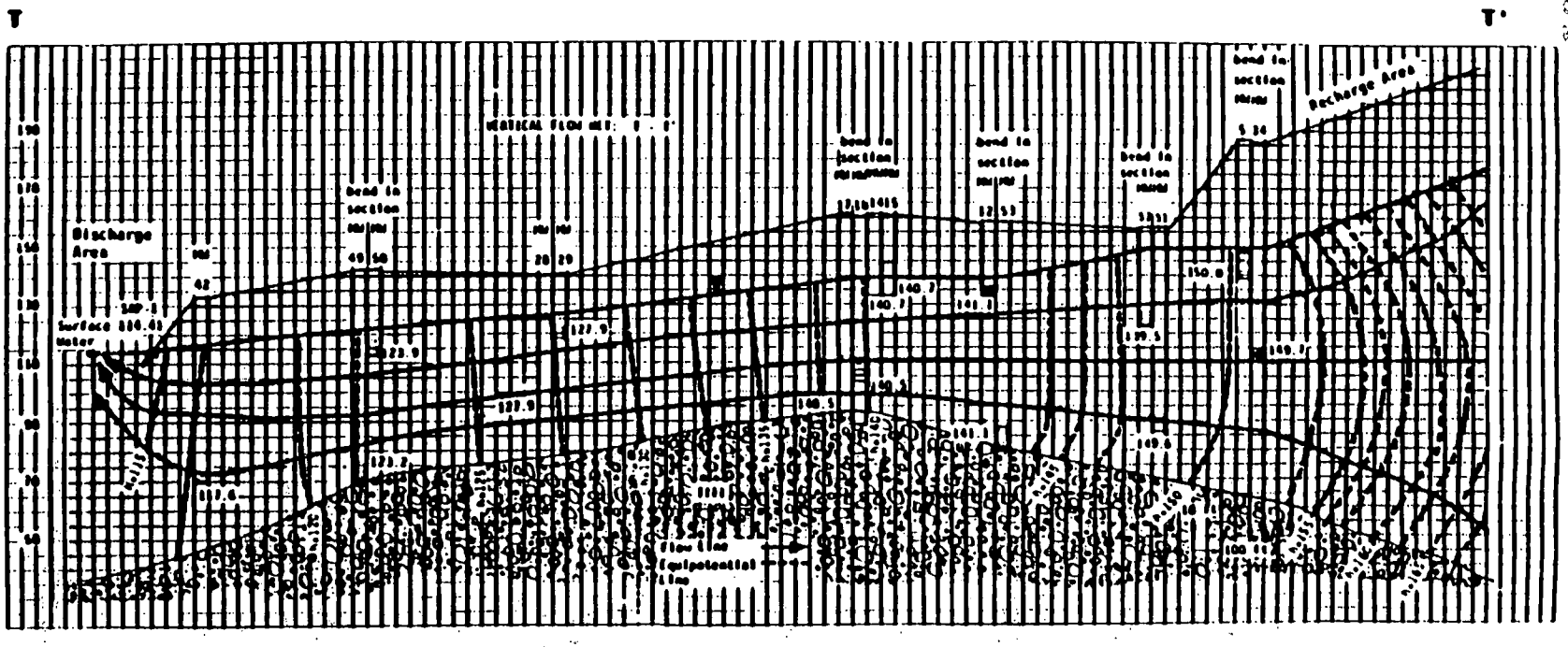

Figure 15-42. Vertical Flow Net T-T'

gradients are not consistently found near the saddle. Hypothesis 3 is feasible and deserves further study. Aerial photographs were examined to identify paved and unpaved areas, but the available ground-water data are insufficient for detailed correlation to these distinct areas. Additional data are needed to construct a more-detailed flow net to further evaluate this hypothesis. Hypothesis 4, which asserts that most of the flow is horizontal, addresses the area of the site where the major portion of ground-water flow occurs. Although it relies on undefined causes to explain fluctuations, it reflects the most logical explanation of the data.

Results

During construction of the flow net and testing of the hypotheses several issues were identified. One of the most important gaps in the study to date is how localized flow at the site fits into the regional ground-water flow regime. Regional flow issues would need to be resolved prior to determining the extent and type of corrective measures, if necessary. The following regional flow issues were identified:

- Geologic information beyond the facility property boundary is necessary to explain the suspected bedrock in the middle of the river directly beside the site to characterize the regional ground-water flow (i.e., to determine the possibility for contamination of regional ground water). The difference in elevation of the top of the bedrock in the river and the top of the bedrock throughout the facility is approximately 120 feet. How can this be explained? Is the bedrock surface irregular or is this rock a glacially-transported boulder exposed in the river? How does this affect regional ground-water flow?

- Data consistently show a downward gradient (i.e., recharge conditions) near the river. This is difficult to explain because rivers in this region are not expected to be losing streams (Heath, 1984). The expected flow direction near a ground-water discharge area, in this case a gaining stream, is upward. Data points showing downward flow near the river are not included in flow net T-T'. (Further investigation of vertical gradients near the river is recommended). If this downward gradient near the river is confirmed, near-water-table contamination could move

downward and contaminate deeper ground water. If deeper, regional contamination must be addressed, corrective measures may be significantly more difficult and extensive.

Other issues deal with localized flow patterns that may affect design of corrective measures. Resolution of these issues will probably not change the overall scope of corrective measures, but would need to be considered in the detailed design.

These localized flow pattern issues are as follows:

- The hydraulic head in the brook is higher than the head in the closest wells in the aquifer, but the water slopes toward the stream. This is inconsistent. If ground water from the site is not discharging into this stream, fewer interceptor wells may be needed.

- Anisotropy must be taken into account in determining the region of flow captured by interceptor wells, drains, etc.

- Till identified as lenses in outwash deposits may actually be continuous with upgradient till, causing the aquifer to flow under confined conditions. Are the till beds isolated lenses or are they continuous? If the till beds in the outwash aquifer are continuous and isolate adjacent zones within the aquifer, they will have the potential of blocking flow to interceptor wells that may be included in the corrective measures plan.

- Vertical gradients of 0.25 and 0.002 in the same geologic unit are presented. Are these gradients accurate and how can they be explained? There could be artificial discharge (pumping) or recharge (possibly from a leaking sewer) near the wells showing a high vertical gradient. The areas labeled discharge areas show no signs of surface water or other surficial evidence of discharge. Artificial recharge and discharge may create areas of relatively constant head, such as where ground water contacts leaky sewers; these areas could limit the growth of cones of influence of any interceptor wells or drains. Also, any contaminated water that may be discharging from pipes should be identified and corrected.

Case Discussion

Further investigation is necessary to resolve the above issues. Regional flow issues should be resolved first. This information would be used to better understand localized flow patterns which would affect the design of corrective measures. The following options for further investigation are suggested:

1. Study the regional geology and hydrogeology. Techniques that could be employed using existing data include review of geologic maps, analysis of well logs, and interpretation of existing surface geophysical data (e.g., gravity and magnetic surveys). Measurement of water level elevations in wells outside the site would also be useful.

2. Conduct a detailed study of the depositional environment of the glacial deposits on the site. This should provide a better understanding of flow patterns.

3. Collect a full-year series of head data at existing wells to differentiate transient from steady-state (e.g., artificial from natural) effects in the measured heads.

4. Conduct multiple-well pumping tests to determine the degree of connectivity of geologic formations using wells at different depths and locations. [Note: this should be done with careful attention to details of well construction so that it is understood exactly what is being measured.]

5. Collect detailed chemical data (including major ions and contaminants) at the existing wells and interpret them to aid in characterizing the flow regime.

6. Drill one or more wells into the bedrock near the river to determine the vertical component of ground-water flow at this location.

Options 1 through 5 above are recommended prior to drilling additional wells in the outwash deposits, unless more wells are needed to delineate the release.

Further single-well hydraulic conductivity tests in the glacial deposits are not recommended at this time. The large-scale flow in the outwash aquifer should be determined by the location and relative degree of continuity of the till versus the sand because the permeability contrasts between the till and sand is so much greater than the variability among the different sands. (See paper by Graham Fogg in Water Resources Research, 22, 679.) Single-well tests would be useful for determing localized hydraulic conductivities of the sand bodies, not their connectivity.

Gathering existing data and constructing an initial vertical flow net proved useful in identifying data gaps in defining ground-water flow, and identified problems due to differing interpretations of the existing data. Determining options for gathering additional data necessary to resolve these issues was based on a qualitative understanding of the ground-water flow regime gleaned from construction of the vertical flow net.

References

Fogg, Graham. Water Resources Research. 22, 679.

Heath. 1984. Ground Water Regions of the U.S. USGS Water Supply Paper No. 2242.

U.S. EPA. 1986. Criteria for Identifying Areas of Vulnerable Hydrogeology, Appendix B: Ground-Water Flow Net/Flow Line Construction and Analysis. Office of Solid Waste. Washington, D.C. 20460.

CASE STUDY 23: PERFORMING A SUBSURFACE GAS INVESTIGATION

Points Illustrated

- Design of a phased monitoring program to adequately characterize the extent and nature of a subsurface gas release.
- The use of ambient air and basement monitoring to supplement monitoring well data.
- The importance of subsurface characterization prior to design of a monitoring network.

Introduction

Gases produced in a landfill will migrate via the path of least resistance. Subsurface, lateral migration of landfill gas can occur due to natural and man-made barriers to vertical gas migration, such as impermeable overlying soil layers, frozen soil, or surface water. Installation of a gas-monitoring well network, in conjunction with sampling in buildings in the area, can be used to determine the need for corrective measures.

Facility Description

The unit in question is a landfill covering approximately 140 acres and bordered by a river on one side and a floodwall on the other. Beyond the floodwall lies a residential area (Figure 15-43). Several factors contribute to the subsurface gas migration problem at this landfill. The site reportedly received large quantities of organic wastes which, when decomposed in the absence of air, produce methane and carbon dioxide gases. The presence of "tight", low permeability soils at the ground surface (12 feet of clayey silt at the surface grading to coarse sand and gravel at a depth of 55 feet) in the residential area, combined with a rapidly rising water table below the landfill due to increased infiltration, restrict the vertical area available for gas migration and encourage lateral movement.

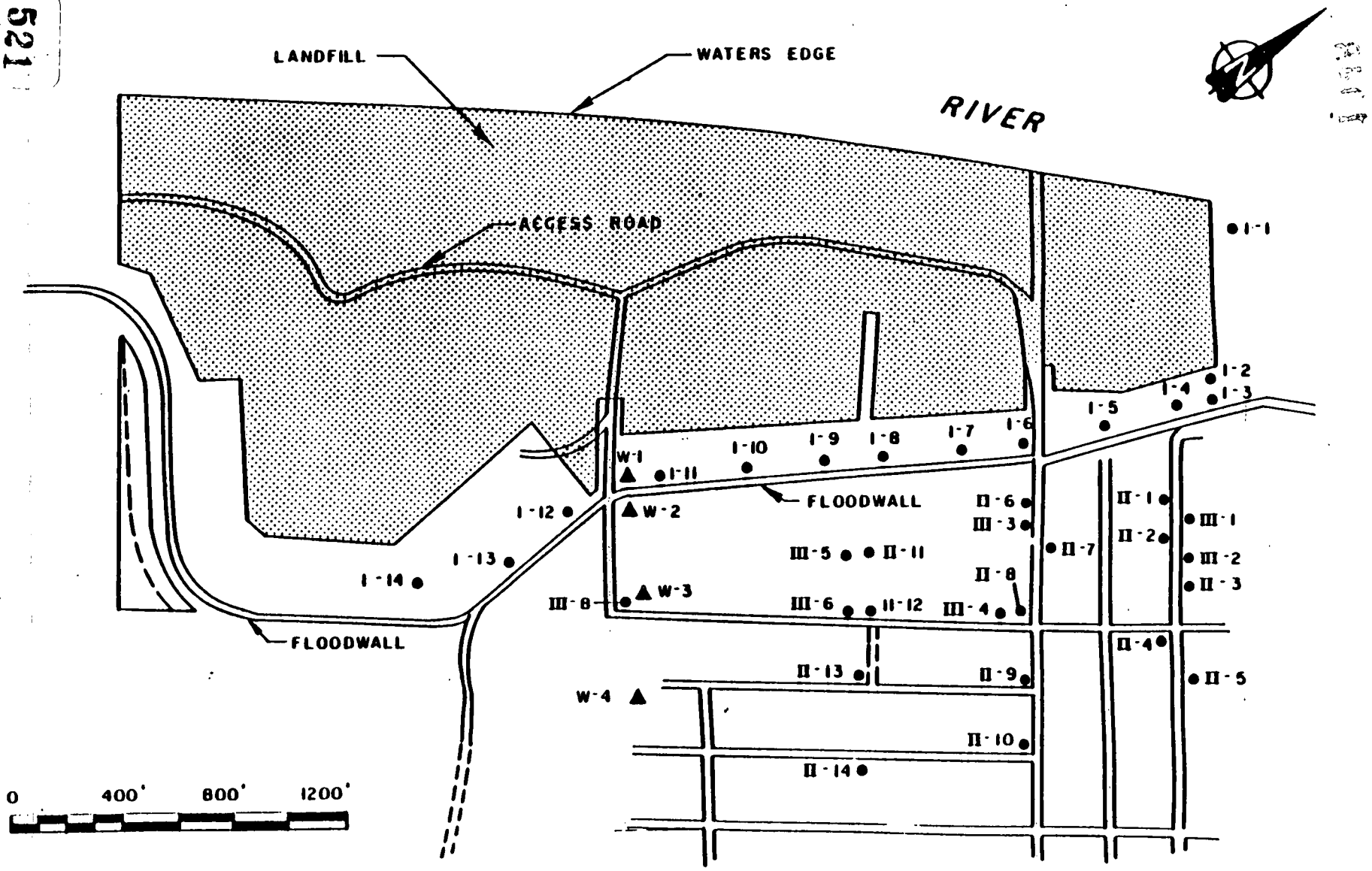

Figure 15-43. Site Plan

Investigation of the gas migration began when foul odors and explosive levels of methane (5 to 15 percent by volume in air) were discovered in the basement of a home approximately 200 feet from the landfill. Residents in the area were evacuated, a sampling network was installed, and monitoring was conducted.

Sampling Program

The sampling was conducted in four phases, an initial screening phase and a more detailed three-phase sampling program. The monitoring network for the initial screening phase consisted of four wells (W1 through W4) aligned perpendicular to the long axis of the landfill, in the direction of (and extending beyond) the house where the gas was initially detected (Figure 15-43). The wells were drilled to an approximate depth of 30 feet below the land surface with the farthest well located about 1000 feet from the landfill boundary. These wells were sampled twice a day for a month. Samples were analyzed for methane and combustible hydrocarbons. The results of this initial monitoring showed average methane levels to be highest at the monitoring well closest to the landfill (30 percent by volume), and roughly grading to below the detection limit at the well farthest from the landfill.

Grab and composite ambient air samples were also taken at the landfill and around houses in the neighborhood where gas was detected during the initial monitoring phase. These samples were analyzed for methane and other combustible hydrocarbons. No gases were detected above normal background levels in any of these above ground samples.

The next phase of monitoring (Phase I of the detailed sampling) involved the installation of 14 new gas monitoring wells (I-1 through I-14 in Figure 15-43). Most of these were placed in a line 250 feet from and parallel to the longitudinal axis of the landfill. Seven of these wells were drilled to an average depth of 55 feet, at least 5 feet below the water table so that ground-water levels could be monitored. The other seven wells averaged 30 feet and did not intercept ground water. As shown in Figure 15-44, each well consists of three separate gas monitoring probes at evenly spaced depth intervals. Each probe was packed in gravel to allow gas to collect in its vicinity. Clay plugs were installed between each probe interval and

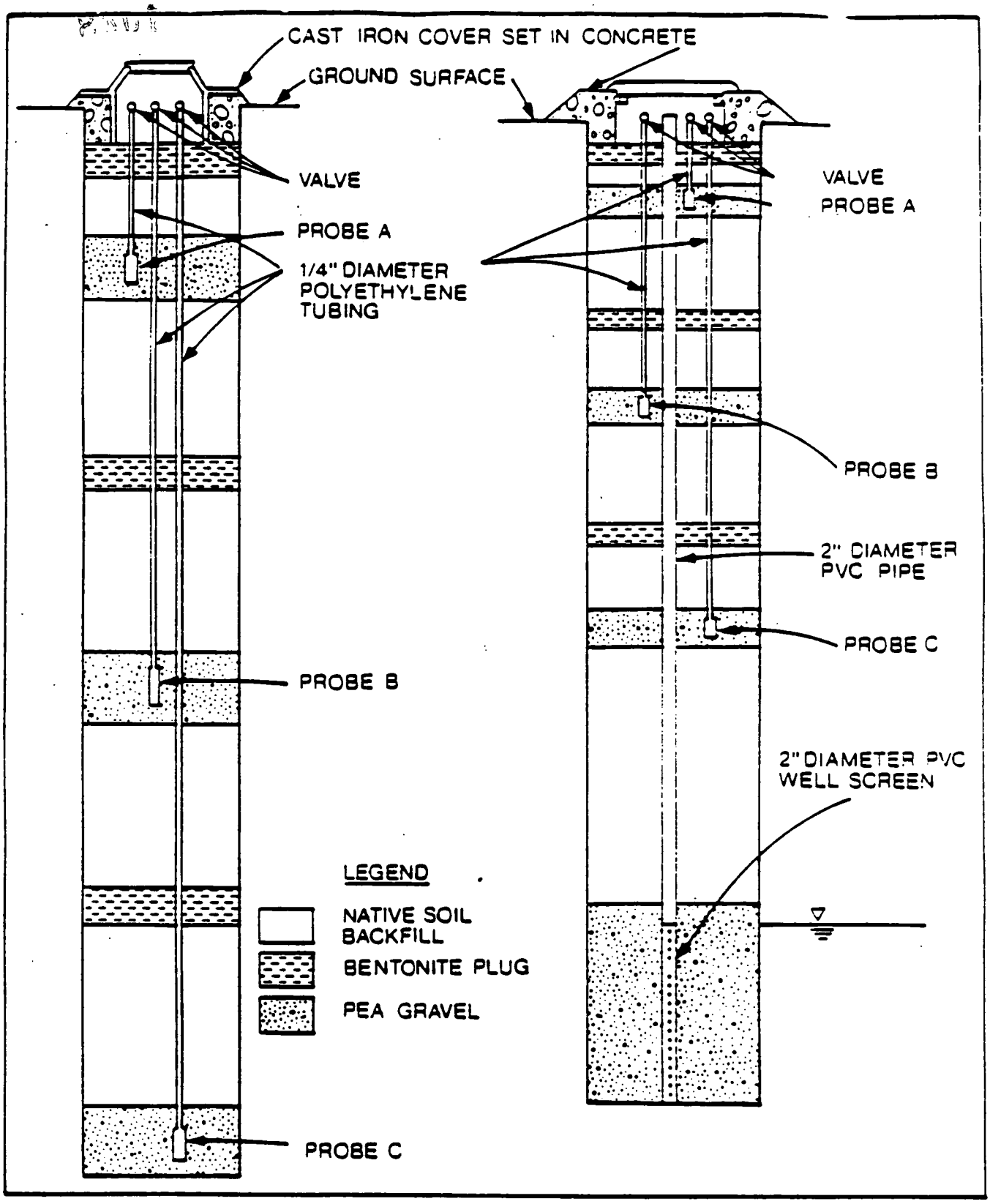

Figure 15-44. Gas Monitoring Well

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between the top probe and the surface to minimize vertical movement of gas in the well. After two months of monitoring the well headspace twice monthly, concern over the high levels of methane that were being measured prompted an expansion of the monitoring well system.

The Phase II monitoring network involved another 14 wells (II-1 through II-14) installed to a depth of 6 feet along three radial lines from the landfill. These wells were monitored twice monthly with the Phase I wells. Methane was not detected at these wells because they were not deep enough to penetrate the clayey silt layer which in this area extended to a depth of 12 feet. Had adequate boring logs been compiled prior to the placement of these wells, the time and money involved in their installation and sampling could have been saved.

Detailed soil boring logs were compiled during the installation of the Phase III wells (III-1 through III-8 in Figure 15-43). These wells were drilled to ground water, averaging 55 feet in depth, were located in the vicinity of the Phase II wells, and were constructed in the same manner as the Phase I wells, with three gas probes placed in each well. The Phase III wells were located from 510 to 900 feet from the landfill. These wells were monitored twice a month for two months concurrently with the Phase I wells. Methane levels at all but two Phase III wells (which are located along the same radial line) exhibited explosive concentrations, ranging up to 67 percent by volume in air. These high concentrations of gas prompted another round of sampling of homes in the vicinity of wells exhibiting high methane concentrations.

Methane and combustible hydrocarbons were measured in basements, crawl spaces, and living areas of 28 homes adjacent to the landfill. All proved to be well below the lower explosive limit of methane.

Wells were then selected based upon proximity to houses exhibiting the highest levels of combustible gases, and sampled to determine gas composition and concentration. The proportion of constituents in the collected gas was similar in all samples analyzed, and concentrations decreased with increasing distance from the landfill.

Ambient air sampling for organic gases at the landfill and in the residential area was also performed at this time and showed low levels of several organic compounds. Air samples collected in houses near the landfill showed the presence of two of the gas components measured in the test wells (methane and ethane).

The gas migration hazard had been sufficiently characterized so that a plan for corrective measures could be developed. This involved the installation of 31 gas extraction wells which were located along a line between the landfill and the residential areas, and a blower system to "pump" the gas out of these extraction wells.

Results

The monitoring program implemented for this case was, for the most part, effective in characterizing the extent and concentrations of subsurface gas contamination. The four initial monitoring wells verified that the landfill was the source of contamination. Phase I monitoring confirmed that the high levels of methane were present at all depths monitored and along the entire length of the landfill. The horizontal location of the Phase II wells, in lines radiating from the landfill, was appropriate, although the lack of subsurface characterization rendered them useless. Phase III sampling established the vertical and lateral extent of subsurface contamination into the residential area.

Throughout the study, ambient air sampling as well as monitoring of homes in the area of concern provided adequate safety control, as well as an additional indication of potential migration of landfill-generated gases.

Case Discussion

Subsurface gas migration can occur when atmospheric ventilation of gases generated in a landfill is insufficient. The gas produced migrates along the paths of least resistance. Conditions restricting release to the atmosphere, such as saturated or tight surficial soils, may force the gas to move laterally over considerable distances.

This case was selected as an illustration of a phased approach to monitoring a subsurface gas release. The results of one phase of monitoring were incorporated into the design of the next phase throughout the study. Monitoring was performed at discrete vertical levels below the surface and at distances from the landfill that were adequate to confirm the extent of the contaminant plume.

The study also illustrates the importance of characterizing subsurface conditions prior to installing monitoring wells. Fourteen unusable wells were installed and then monitored for two months because of insufficient preliminary soil (stratigraphic) characterization.

The use of ambient and basement monitoring for gas to supplement monitoring well data is also noted in this case study. The location of new wells can be based in part on readings from these sources.

CASE STUDY 24: USE OF A SUBSURFACE GAS MODEL IN ESTIMATING GAS MIGRATION AND DEVELOPING MONITORING PROGRAMS

Point Illustrated

- Predictive models can be used to estimate the extent of gas migration from a suspected subsurface source. This information can be used to estimate human exposure and to determine appropriate locations for monitoring wells and gas collection systems.

Introduction

Methane is a common landfill gas and is often used as an indicator of landfill gas migration. The subsurface methane predictive model, described in Volume II, Appendix D of this document, will yield a methane concentration contour map and predict the distance that methane will migrate. The model consists of a series of charts developed by imposing a set of simplifying assumptions on a general methane migration computer model.

A methane migration distance prediction chart is used to find a preliminary migration distance based on the age of the site and the soil type. The remaining charts are used to find correction factors which are in turn used to adjust the migration distance. These factors are based upon site characteristics (e.g., depth of the waste).

Facility Description

The unit is located on a 583-acre site in a suburb of a major metropolitan area. Figure 15-45 shows the site layout. The landfill itself occupies 290 acres. 140 acres of the landfill were used for the disposal of hazardous wastes. Both hazardous and nonhazardous wastes were disposed at the site from 1968 to 1984. Hazardous waste disposal ended in 1984. The disposal of sewage treatment sludges and municipal refuse continues. As seen in Figure 15-45, residential development has taken place with houses now bordering the facility to the south. A population of 30,000 to 40,000 people reside within a mile radius of the landfill center.

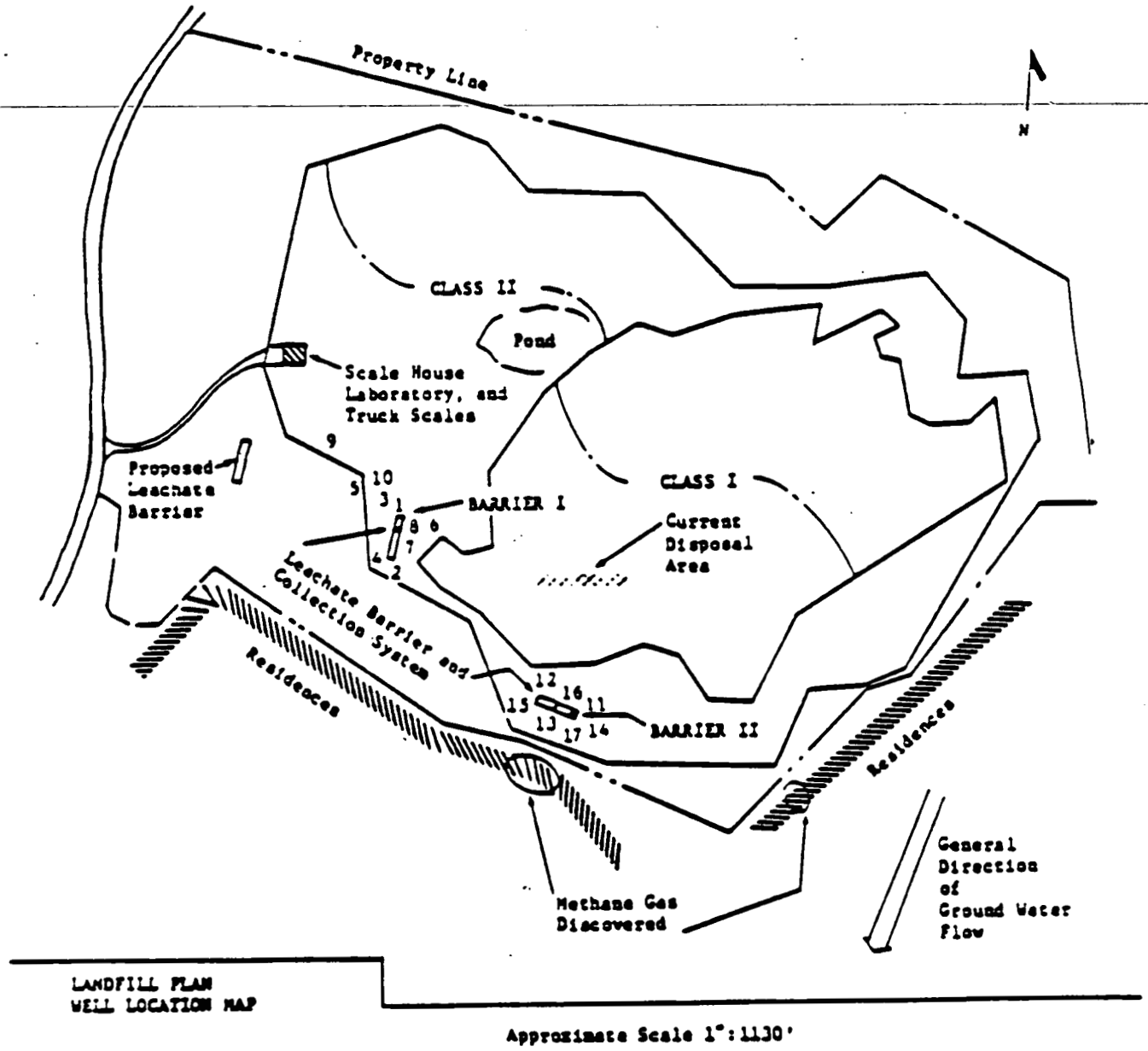

Figure 15-45. Facility Map

The unit is a V-shaped fill overlying sediment and bedrock. The rock type is a poorly consolidated, fractured sandy silt offering no lithologic barrier to gas migration. The shape of the water table has not been established. Also unknown are the possible effects of local, permeable formations such as sand lenses, faults, etc.

The warm climate at the site encourages rapid degradation of organic wastes and therefore rapid gas production. Site characteristics suggest that vertical gas migration is not hindered. However, the compaction of the fill cover by truck traffic combined with the rapid production of gas has forced lateral migration through the fractured sandy silt.

Applying the Subsurface Methane Predictive Model

The subsurface methane predictive model allows the development of a subsurface methane concentration contour map. The model predicts the distance methane will migrate from a unit based on its age, depth, soil type, and environmental factors. A contour map for two different methane concentrations, 5 and 1.25 percent, is predicted. The likelihood of human exposure can be estimated from the location of the contours with respect to on-site and off-site structures.

Application of the model involves three steps. The first step is the prediction of gas migration distances, based on the age of the landfill and the local soil type. The unit of interest is 18 years old and has sandy soils. Figure 15-46 shows the uncorrected methane migration distances for various soils over time. From Figure 15-46, the uncorrected migration distances for the subject site are 165 feet and 255 feet for 5 and 1.25 percent methane concentrations, respectively.

The second step in applying the model involves the application of a correction factor to the migration distances based on waste depth. The deeper the waste, the greater the opportunity for subsurface migration. Figure 15-47 is used to find the correction factors for depth. For the subject waste unit the depth is 25 feet, which corresponds to a correction factor of 1.0 for both concentrations.

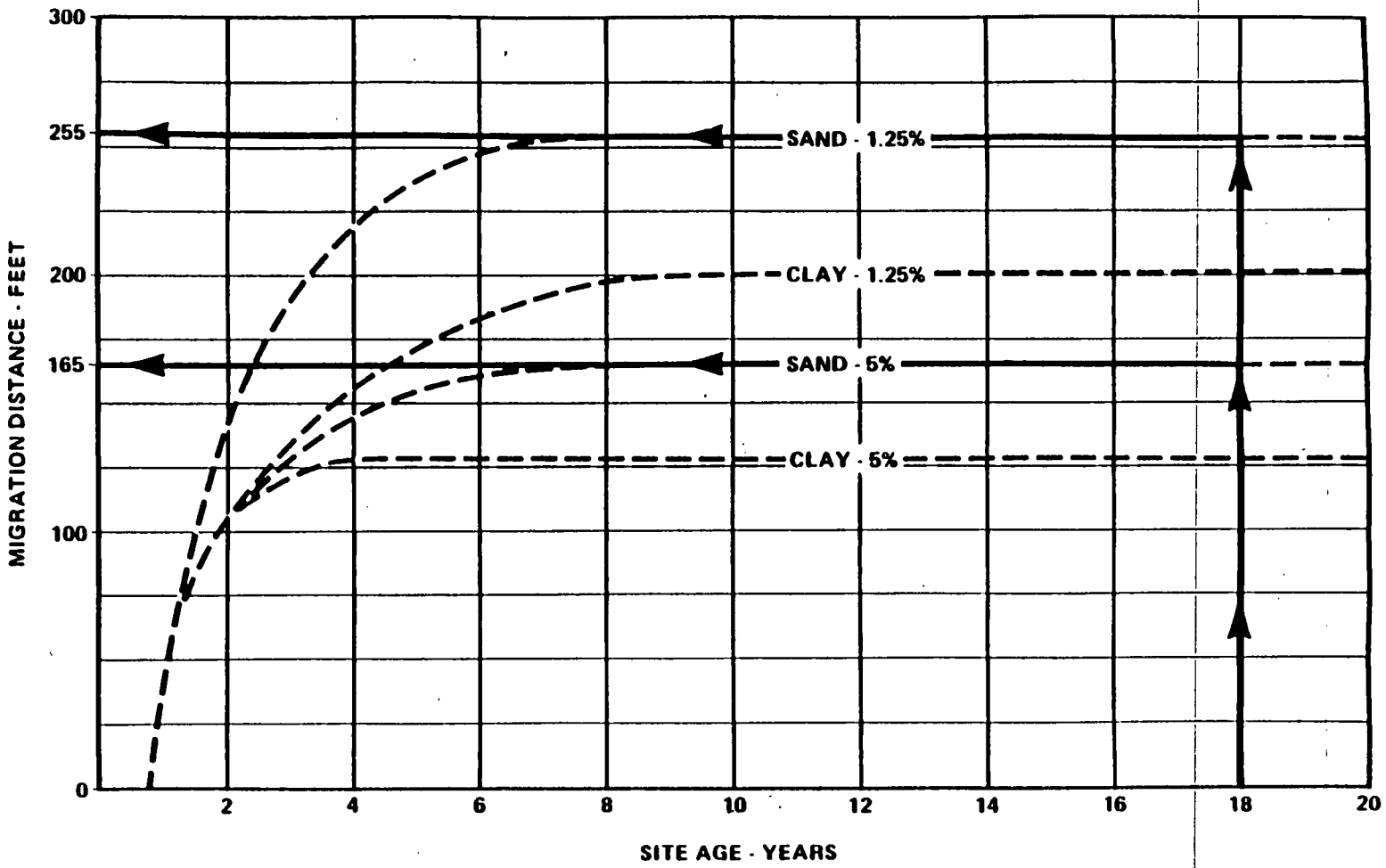

Figure 15-46. Uncorrected Migration Distances for 5 and 1.25% Methane Concentrations

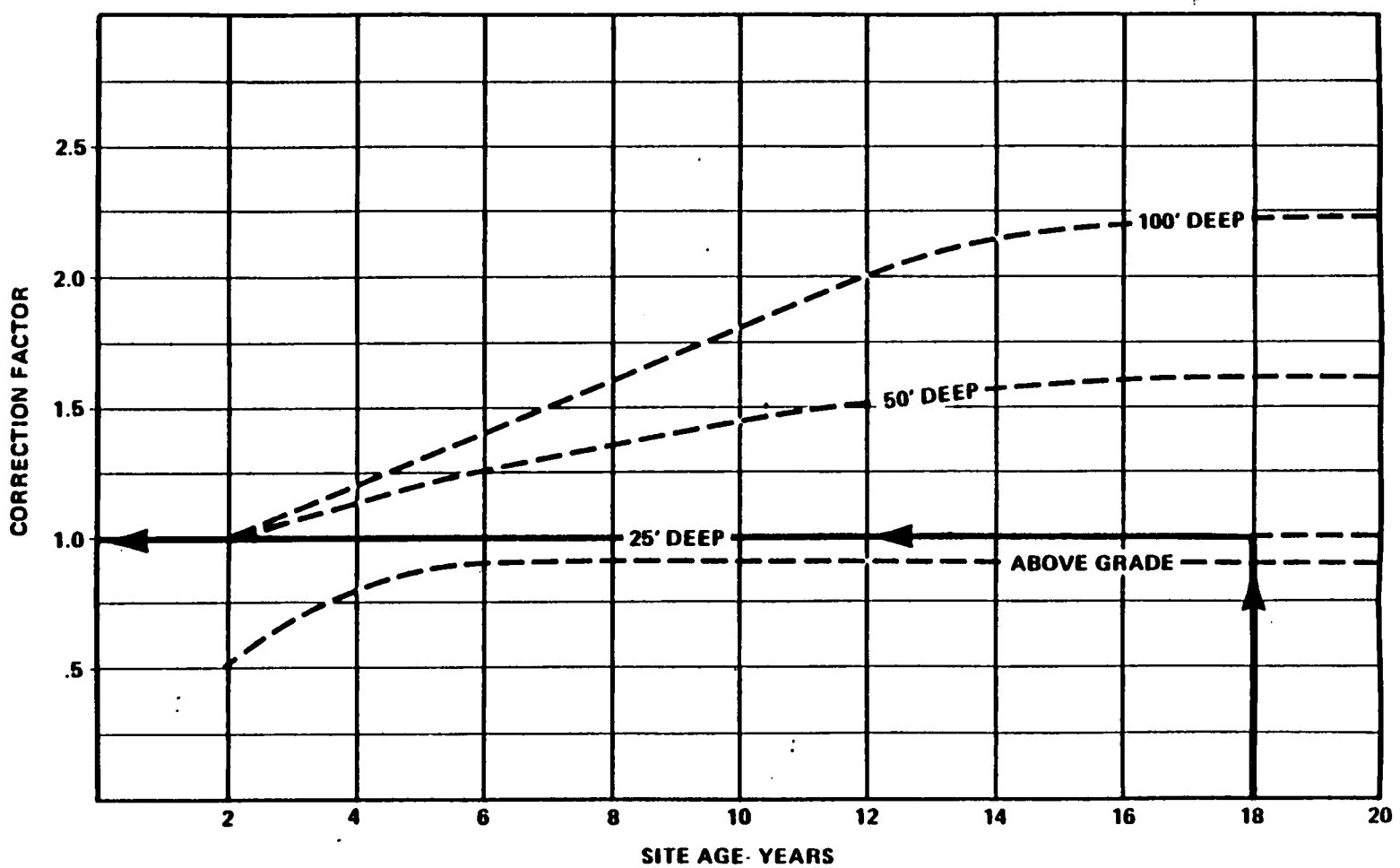

Figure 15-47. Correction Factors for Landfill Depth Below Grade

The final step in applying the model is the correction of migration distances based on surface venting conditions. The following equation is used to calculate the adjusted correction factor, ACF:

ACF = [(ICF-1)(fraction of site which is impermeable)] + 1

The impervious correction factor, ICF, is obtained from Figure 15-48. In the above equation, ICF is adjusted to account for the fraction of time the solid is saturated or frozen and the fraction of the land area that is impermeable due to natural or man-made barriers. If corrections for both time and area are required, the fractions are additive. From Figure 15-48, the ICF for a unit 18 years old and 25 feet deep is 2.4. Site charcteristics together with weather conditions indicate a value of 0.4 for the fraction of impermeable area. Substituting these values into the above equation yields an adjusted correction factor of:

ACF = [(2.4-1)(0.4)] + 1 = 1.56.

Results

Table 15-14 summarizes the results from steps one through three of the model application. The predicted migration distances for methane are found by multiplying the uncorrected distance from step one by the correction factors from steps two and three. The predicted distances of travel for methane are 255 feet and 395 feet for 5 and 1.25 percent concentrations, respectively.

TABLE 15-14

MODEL RESULTS

Methane Concentration (percent)	Uncorrected Distance (ft)	Correction for Depth	Correction for Venting	Corrected Distance (ft)
5	165	1.0	1.56	255
1.25	255	1.0	1.56	395

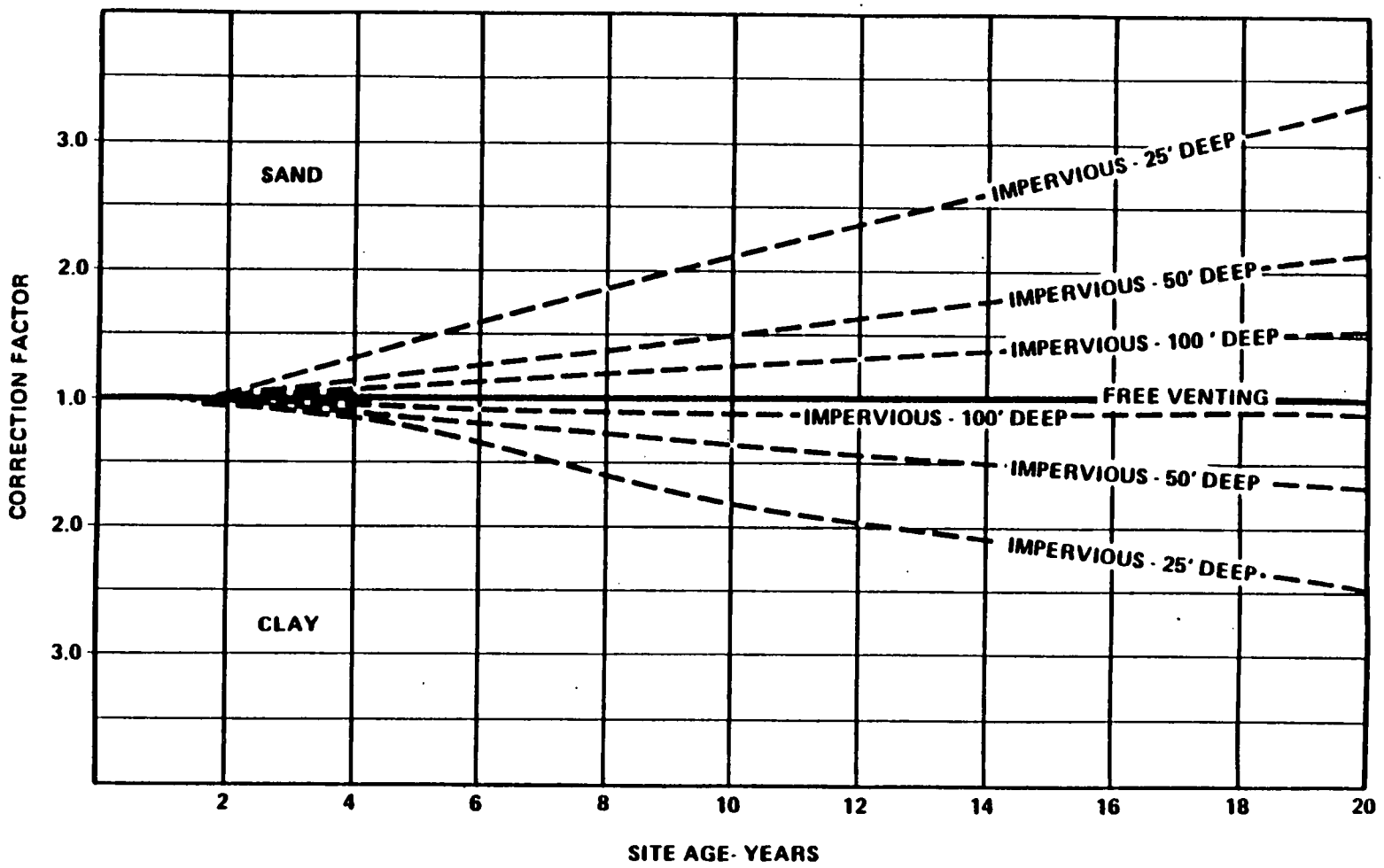

Figure 15-48. Impervious Correction Factors (ICF) for Soil Surface Venting Condition Around Landfill

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Case Discussion

Figure 15-49 is a methane concentration contour map developed from the predicted travel distances. The map indicates that the possibility of human exposure to landfill gas is high. Landfill gas is known to be present and well drilling operations at the landfill have caused minor explosions. The monitoring wells along the facility perimeter and testing in nearby homes indicate that gas has migrated off site. Both the 5 percent and 1.25 percent methane contours enclose homes evacuated because of gas accumulation. Measures have been taken to mitigate the immediate problems and the landfill operators have installed additional gas collection wells and extended the monitoring system.

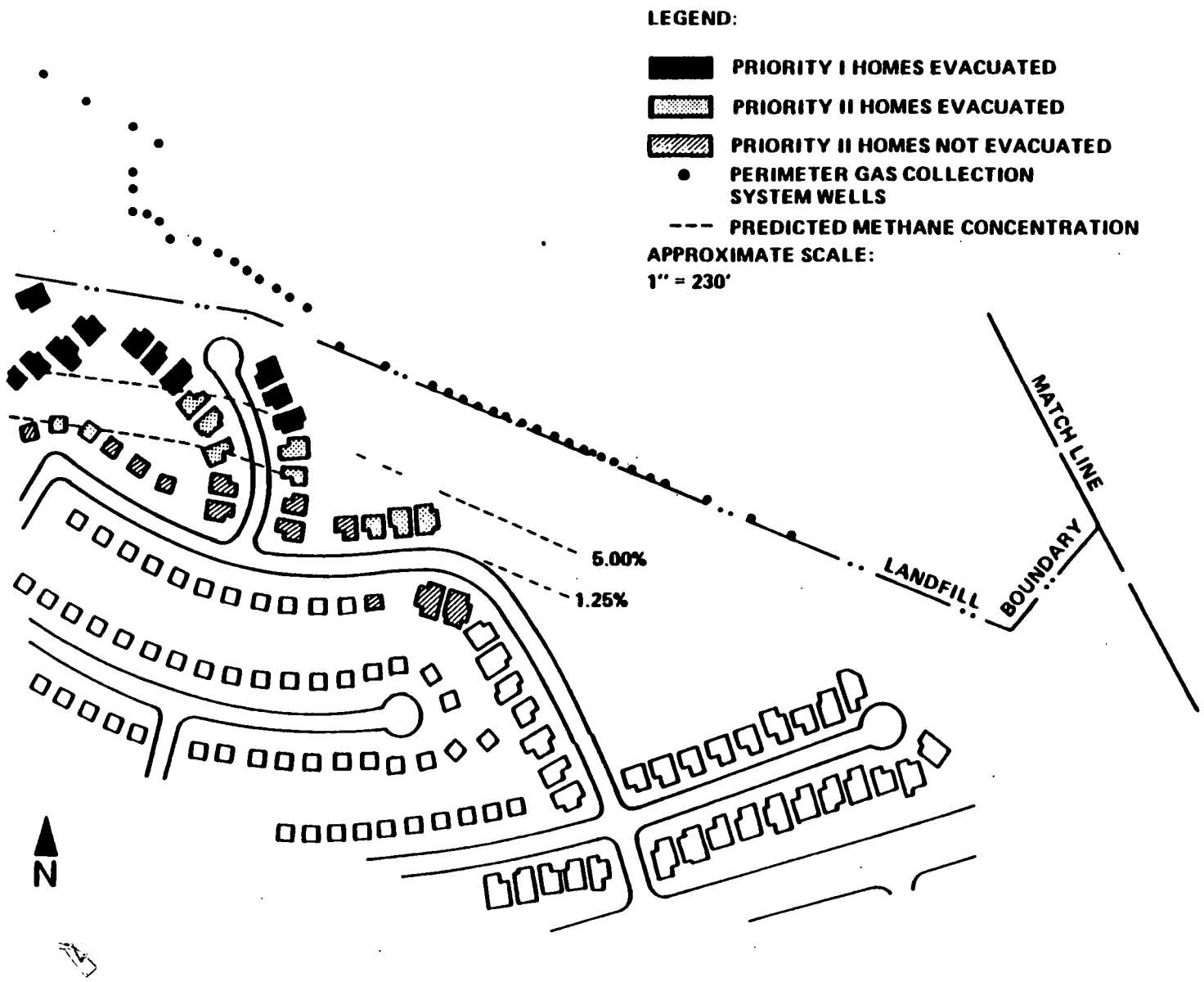

Figure 15-49. Landfill Perimeter Gas Collection System Wells

CASE STUDY 25: USE OF METEOROLOGICAL/EMISSION MONITORING DATA AND DISPERSION MODELING TO DETERMINE CONTAMINANT CONCENTRATIONS DOWNWIND OF A LAND DISPOSAL FACILITY

Point Illustrated

- How to use meteorological/emission monitoring data and dispersion modeling to estimate contaminant concentrations.

Introduction

Concern over possible vinyl chloride transport into residential areas adjacent to a land disposal facility prompted initiation of this study. As a followup to a screening assessment (involving emission modeling) a survey and emission monitoring program with the application of an air dispersion model were used to assess potential health hazards.

Facility Description

The facility is a landfill which has been in operation since 1963. The facility occupies an area of 583 acres, of which 228 acres contain hazardous and municipal waste. The facility and surrounding terrain is hilly with elevations ranging from 600 to 1150 feet above mean sea level. Residential areas are located immediately adjacent to the south and southeast facility boundaries, as shown in Figure 15-50.

The facility previously received waste solutions from the synthesis of polyvinyl chloride which included the vinyl chloride monomer. Gas is generated by municipal waste decomposition and chemical waste volatilization. The primary air release from the particular unit is vinyl chloride. A gas collection system has not been installed for this unit.

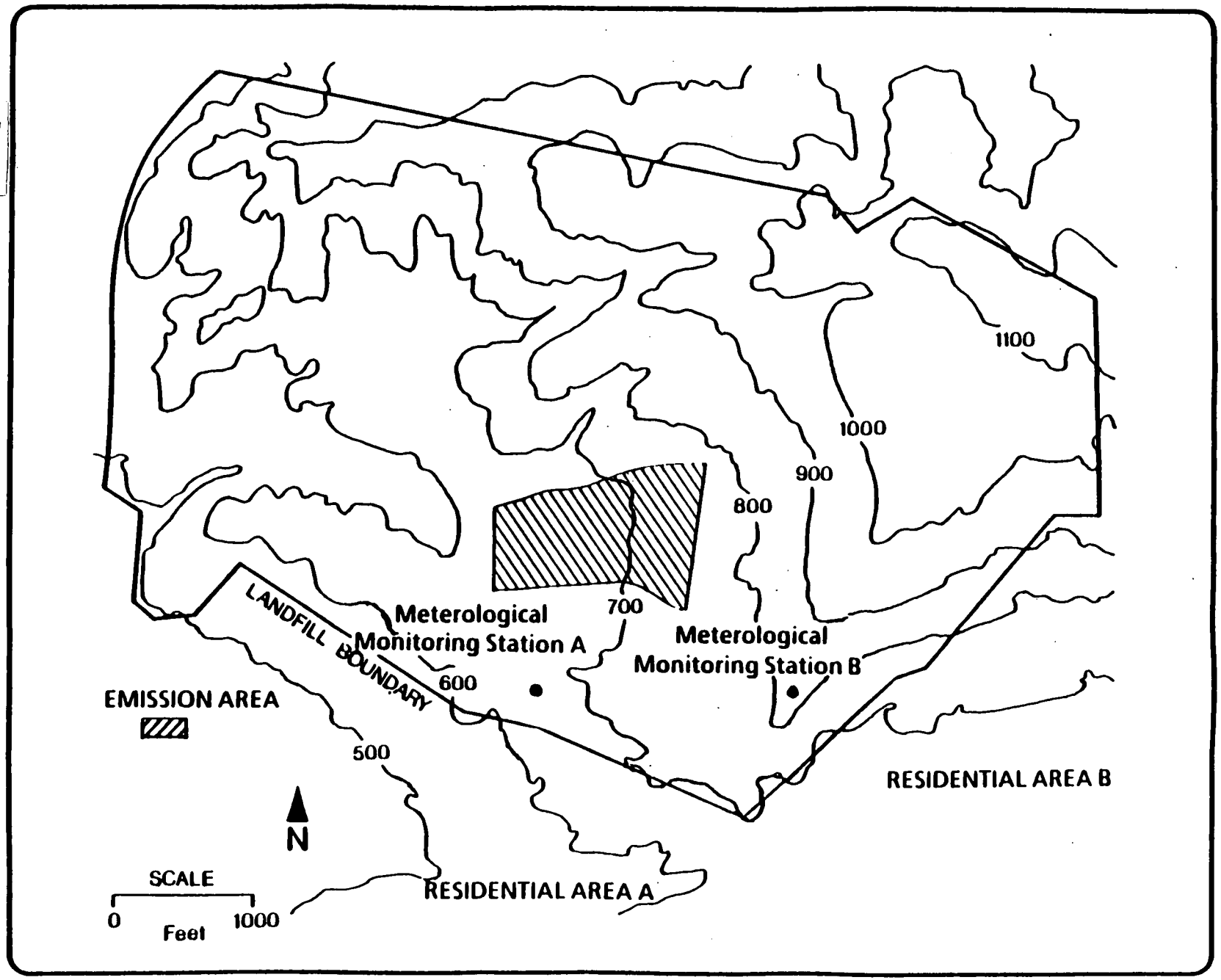

Figure 15-50. Site Map Showing Location of Meteorological Sites A and B (Adapted from Baker & Mackay, 1985)

Program Design/Data Collection

A screening assessment (based on emission/dispersion modeling) was conducted to evaluate vinyl chloride emissions from the landfill. Evaluation of these results indicated that emission monitoring should be conducted to more accurately quantify the release. An isolation flux chamber was used to measure vinyl chloride emissions during a three-day period in August. This sampling period was selected based on the screening assessment results to represent worst case emission and dispersion conditions.

An on-site meteorological survey program was also conducted to characterize wind flows at this complex terrain site. Two meteorological stations were deployed to evaluate wind flows, as influenced by complex terrain, which may impact the two adjacent residential areas (see Figure 15-50.) A one-month data collection period during August was conducted to characterize on-site wind and stability patterns during worst-case, long-term emission/dispersion conditions. Although the facilty is located in complex terrain, the diurnal wind pattern during the meteorological survey was very consistent from day to day. Therefore, the one-month meteorological monitoring period was adequate for this RFI application.

Program Results/Data Analysis

The emission monitoring and meteorological monitoring data were used as input for dispersion modeling. The wind patterns were different for each of the on-site meteorological stations (see Table 15-15). Therefore, two sets of modeling runs were conducted (meteorological station A data were used to estimate concentrations at residential area A and meteorological station B data were used to estimate concentrations at residential area B).

The dispersion modeling results indicated that estimated concentrations at both residential areas were significantly below the RFI health criteria. Therefore, followup air release characterizations were not necessary and information was sufficient for RFI decision making.

TABLE 15-15

SUMMARY OF ON-SITE METEOROLOGICAL SURVEY RESULTS

	Station A	Station B
Prevailing daytime wind direction	S	SW
Prevailing nighttime wind direction	NNE	ENE

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Case Discussion

Emission sampling was appropriate for this application because of the uncertainties associated with emission rate modeling for landfills (including uncertainties in emission modeling inputs such as the waste composition and spatial distribution). The isolation flux chamber technique provided a basis for direct measurement of vinyl chloride emission rates for dispersion modeling input.

The conduct of an on-site meteorological monitoring survey provided the required wind and stability input for dispersion modeling. The use of multiple meteorological towers for this application was necessary to characterize wind flow patterns in complex terrain and to account for off-site exposure at two residential areas subject to different wind conditions. The combination of emission monitoring, meteorological monitoring and dispersion modeling provided an effective air release characterization strategy for this RFI application.

References

Baker, L.W. and K.P. MacKay. 1985. Screening Models for Estimating Toxic Air Pollution Near a Hazardous Waste Landfill. Journal of Air Pollution Control Assocation, 35:11.

CASE STUDY 26: USE OF METEOROLOGICAL DATA TO DESIGN AN AIR MONITORING NETWORK

Points Illustrated

- How to design an air monitoring program
- How to conduct an upwind/downwind monitoring program when multiple sources are involved.

Introduction

A screening assessment (based on emission/dispersion modeling) commensurate with RFI guidance was conducted to characterize hazardous air constituents being released from a wood treatment facility. Evaluation of these screening results indicated that it was necessary to conduct a monitoring program to more accurately quantify air emissions from units at the facility. Meteorological data were first collected to determine the wind patterns in the area. The wind direction data with the locations of the potential emission sources were then used to select upwind/downwind air sampling locations.

Facility Description

The site is a 12-acre wood treatment facility located in a flat inland area of the southeast. Creosote and pentachlorophenol are used as wood preservatives; heavy metal salts have been used in the past. Creosote and pentachlorophenol are currently disposed in an aerated surface impoundment. Past waste disposal practices included treatment and disposal of the metal salts in a surface impoundment, and disposal of contaminated wood shavings in waste piles. The constituents of concern in the facility's waste stream include phenols, cresols, and polycyclic aromatic hydrocarbons (PAH) in the creosote; dibenzodioxins and dibenzofurans as contaminants in pentchlorophenol; and particulate heavy metals. The potential emission sources (Figure 15-51) include the container storage facility for creosote and pentachlorophenol, the wood treatment and product storage areas, the aerated surface impoundment for the creosote and pentachlorophenol wastes, and the contaminated soil area which previously contained both the surface

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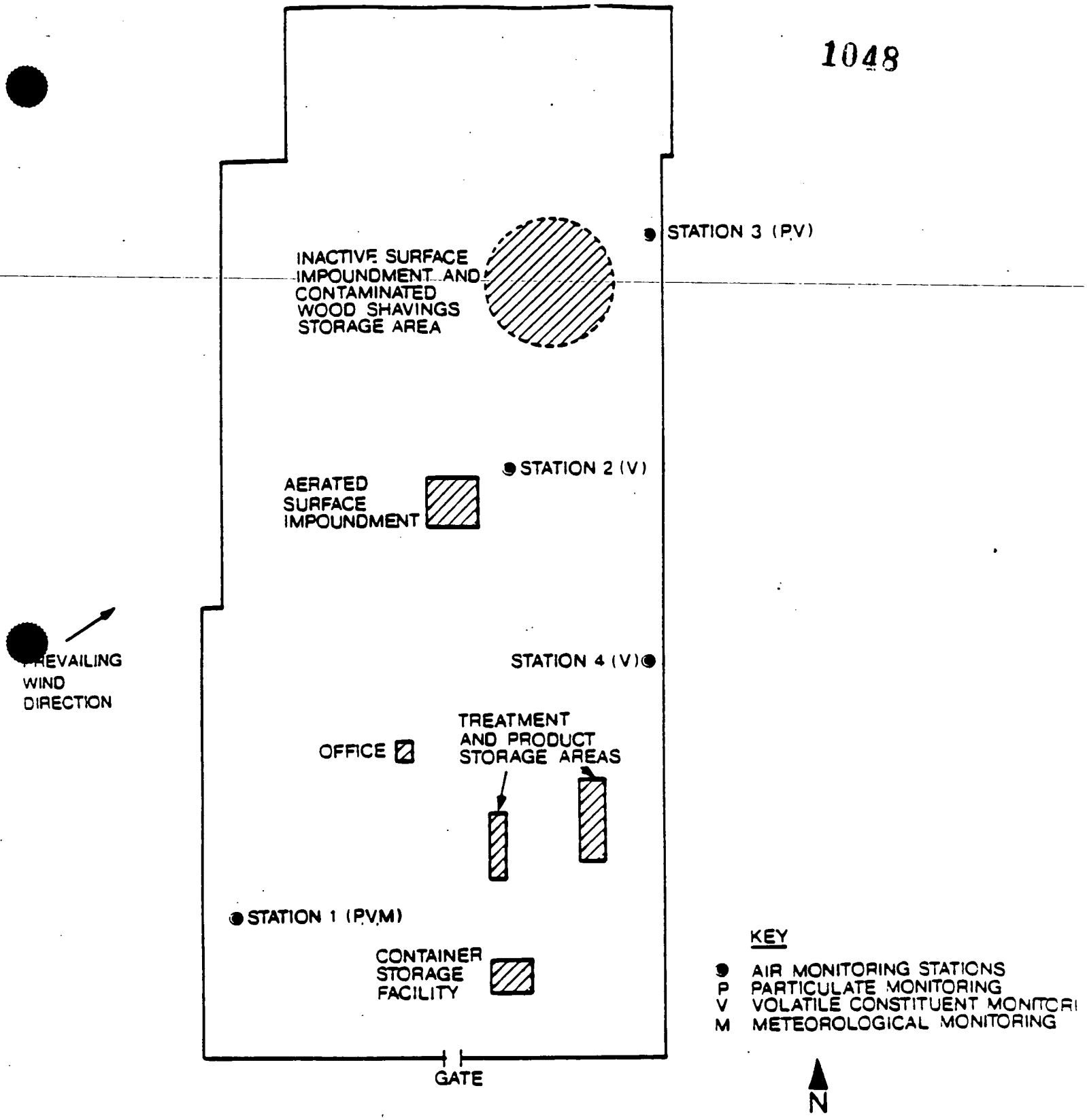

Figure 15-51. Site Plan and Locations of Air Monitoring Stations

impoundment for treating the metal salts and the wood shavings storage area. Seepage from these waste management units has resulted in documented groundwater and surface water contamination.

The area surrounding the facility has experienced substantial development over the years. A shopping center is now adjacent to the eastern site perimeter. This development has significantly increased the number of potential receptors of air releases of hazardous constituents.

Program Design/Data Collection

Preliminary Screening Survey--

A limited-on-site air screening survey was first conducted to document air releases of potentially hazardous consituents, to prioritize air emission sources, and to verify screening assessment modeling results and the need to conduct a monitoring program. Total hydrocarbon (THC) levels were measured with a portable THC analyzer downwind of the aerated surface impoundment, wood treatment area, and product storage area. Measurements were also made upwind of all units to provide background concentrations. Because THC levels detected downwind were significantly higher than background levels, a comprehensive monitoring program to characterize releases to the air was designed and implemented.

Waste Characterization--

To develop an adequate monitoring program, the composition of wastes handled in each waste management unit was first determined to identify which constituents were likely to be present in the air releases. Existing water quality data indicated contamination of ground water with cresols, phenol, and PAHs and of surface water with phenols, benzene, chlorobenzene, and ethylbenzene. A field sampling program was developed to characterize further the facility's waste stream. Wastewater samples were collected from the aerated surface impoundment and soil samples were collected from the heavy metal salt waste treatment/disposal area. Analytical data from this sampling effort confirmed the presence of the constituents previously identified. Additional constituents detected included toluene and xylenes in surface impoundment wastes, and arsenic, copper, chromium, and zinc in the treatment/disposal area.

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Based on their individual emission potentials and potentials for presenting health and environmental hazards, the following constituents were selected for measurement in the air monitoring program:

Volatile/semi-volatile constituents:	toluene, benzene, total phenols, pentachlorophenol, PAHs, cresols
Particulate constituents:	aresenic, copper, chromium, zinc.

Meteorological Data Collection--

Meteorological information is critical for designing an air monitoring program because stations must be located both upwind and downwind of the contaminant sources. Therefore, a one-month meteorological monitoring survey was conducted at this flat terrain site. The survey was conducted under conditions considered to be representative of the summer months during which air samples would be collected. Summer represented worst-case conditions of light steady winds and warm temperatures. The collected meteorological data showed that the local wind direction was from the southeast. No well-defined secondary wind flows were identified.

Initial Monitoring--

Alternative methods were considered for monitoring emissions from the aerated surface impoundment and contaminated storage area. Direct emission measurements (such as use of isolation flux chambers) would not be practical for aerated ponds or for monitoring particulate emissions from area sources. Therefore, an air monitoring program with samplers located in proximity to the other units of concern was selected for this application.

The on-site meteorological survey data were used with the EPA atmospheric dispersion model, ISC (Industrial Source Complex Model), to estimate worst-case air emission concentrations and to help determine the locations for the air sampling stations. The ISC model was used because it is capable of simulating conditions of point and non-point source air emissions. Using the established southeast wind direction, maximum downwind concentrations were predicted for different

meteorological conditions (e.g., wind speed). Upwind background stations and downwind monitoring stations were selected based on the predicted dispersion pathways. Because the releases from the individual waste management areas overlapped, the model also provided a means for separating the incremental contamination due to each source.

Figure 15-51 shows the locations of the selected sampling stations. Station 1 is the upwind background station. Here background volatile concentrations, particulate concentrations, and meteorological conditions were monitored. Stations 2 and 4 were located to identify volatile emissions from the aerated surface impoundment and wood treatment/product storage areas, respectively. Station 3 was located downwind of the inactive surface impoundment/wood shavings disposal area. This station was sited to document releases from these waste management units and to document worst-case concentrations of volatiles and particulates at the facility property boundary. For this application the locations of Stations 2, 3 and 4 were adequate to characterize air concentrations at both the unit boundary as well as the facility property boundary (due to the proximity of these two boundaries in the area downwind, based on the prevailing wind direction, of the units of concern). A trailer-mounted air monitoring station was used to supplement the permanent stations and to account for any variability in wind direction.

Sample Collection--

The air quality monitoring was conducted over a three-month period during the summer. Meteorological variables were measured continuously on site throughout the study. Air samples were taken over a 24-hour period approximately every six days. The sampling dates were flexible to insure that worst-case conditions were documented.

Volatile and semi-volatile constituents were sampled by drawing ambient air through a sampling cartridge containing sorbent media. A modified high volume sampler consisting of a glass fiber filter with a polyurethane foam backup sorbent (EPA Method TO4) was used to sample for total phenols, pentachlorophenol, and PAHs. Benzene and toluene were collected on Tenax sampling cartridges (EPA

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Method TO1) and cresol was collected on silica gel cartridges (NIOSH Method Z001). Particulates were collected on filter cassettes using high-volume samplers.

In addition to the constituents previously discussed, Appendix VIII metals were analyzed on the first few sets of samples. These analyses were conducted to identify air releases of constituents other than those known to be present. The results indicated that no additional constituents were present in significant concentrations, so the additional analyses were dropped for the remainder of the study.

Program Results/Data Analysis

Standard sampling/analytical methods were available for all the target monitoring constitutents. Analytical detection limits were below specific health and environmental criteria for all constituents except cresol. The high analytical detection limit for cresol which exceeded reference health criteria complicated data analysis. This difficulty was handled by the routine collection and analysis of waste water samples during the air monitoring program. These data were used to estimate cresol levels in the air by comparing its emission potential to the other air monitoring constituents which have relatively low detection levels.

Analytical results obtained during this sampling program established that fugitive air emissions significantly exceeded reference health criteria. Source control measures were implemented to reduce emission concentrations below health criteria levels. Subsequent air monitoring was conducted at the same stations used previously on a weekly basis immediately after implementation of the remedial measures, and on a quarterly basis thereafter.

Case Discussion

This case illustrates a sequence of tasks which were taken to design an air monitoring program at a site with multiple air emission sources. An initial field survey was conducted to identify local prevailing wind patterns and to identify potential downwind receptors of fugitive air emissions. The meteorological survey results were used to design an effective monitoring network. Monitoring station locations were selected to obtain background conditions and to document air releases downwind of each emission source. Also, the monitoring strategy included

use of a portable sampling station to provide flexibility in sampling locations to account for variation in wind direction. Spatial variability in air concentration was assessed with the aid of an air dispersion model to assist in data interpretation.

Air emissions data showed an air release of hazardous constituents significantly above health crtiteria levels. Remedial measures were implemented, and periodic subsequent monitoring was conducted to insure compliance with the health criteria.

References

Methods T01 and T04, Compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air, 1984, EPA-600/4-84-041.

Method Z001, NISOH Manual of Analytical Methods, 1984, National Institute of Occupational Safety and Health.

CASE STUDY 27: DESIGN OF A SURFACE WATER MONITORING PROGRAM

Point Illustrated

- When designing a surface water monitoring program, site-specific sediment and suspended solids information should be considered.

Introduction

Designing a surface water monitoring program to determine the extent of contamination involves identifying the potential waste sources, the contaminants likely to be present in each waste stream, and the flow paths by which the contaminants could reach surface waters. The fate of the contaminants once they reach the surface water must also be considered when selecting sampling stations and parameters to be measured. The example described here illustrates the design of a monitoring program for a river system.

Facility Description

A facility which processed zinc, copper and precious metals from ores operated along a river for five years. The plant was closed after being cited for repeated fish kills which were reportedly due to failures of a tailings pond dike. At present, the site is covered with tailings containing high concentrations of copper, zinc, cadmium, arsenic and lead. There is no longer a tailings pond.

Site Setting

The site is located on coarse colluvium (hill-slope deposits of weathered bedrock) and fine-grained alluvium. These deposits are typically 50 feet thick. Metamorphic rock (phyllite) underlies the unconsolidated materials. Ground water moves laterally in the gravel formations from the steep valley walls towards the river.

The site is about 400 feet from the river. Two drainage ditches cross the lower portion of the site and merge prior to leaving the site. The ditch carries the

combined flow and discharges directly into the river (Figure 15-52). No other tributaries enter the river within two miles of this location.

Sampling Program

A surface water monitoring program was designed as part of the Phase I remedial investigation to determine the extent of contamination in the river. Existing data from a reconnaissance visit had shown high concentrations of metals in the drainage ditch sediments (e.g., 5,170 mg/kg Cu and 11,500 mg/kg Zn). Ground water data from the plant's well showed concentrations of Cu (7 µg/l) and Zn (54 µg/l). The contribution of metals to the river by ground-water discharge at the site was considered to be relatively small.

Based on a review of the plant history and the available water quality and sediment data, a monitoring program was designed. The potential pathways by which metals could reach the river appeared to be direct discharge from the drainage ditch, seepage of contaminated ground water, and storm water runoff. Plant records indicated that typical flows in the drainage ditch at its confluence with the river varied from 1 to 3 cubic feet per second (cfs) in the spring. During extreme flood conditions, the flow in the ditch exceeded 20 cfs. In the summer, flows in the drainage ditches at all locations were less than 0.5 cfs. Resuspension of contaminated sediments in the ditches during storm runoff appeared to be the most likely pathway for metals to reach the river. The specific metals of concern were identified as As, Cd, Cu, Pb and Zn based on the processes used at the plant and the composition of the ores which contained some arsenopyrites (As, Cu), galena (Pb), and sphalerite (Zn, Cd).

The available soil and water quality data from the reconnaissance visit were reviewed to determine the likely fate of the metals. Soils in the area were circumneutral (pH = 6.5) and contained about 0.5 percent organic matter by weight. Thus the metals, particularly Pb, would be expected to adsorb onto the soil particles. In the on-site tailings piles, the pH of core samples ranged between 3.3 and 4.9. Low soil pH values had been measured in sediments in the drainage ditch just downgradient of the tailings pile. The pH of the river during the reconnaissance was 6.9. The suspended solids concentration was 10 mg/l.

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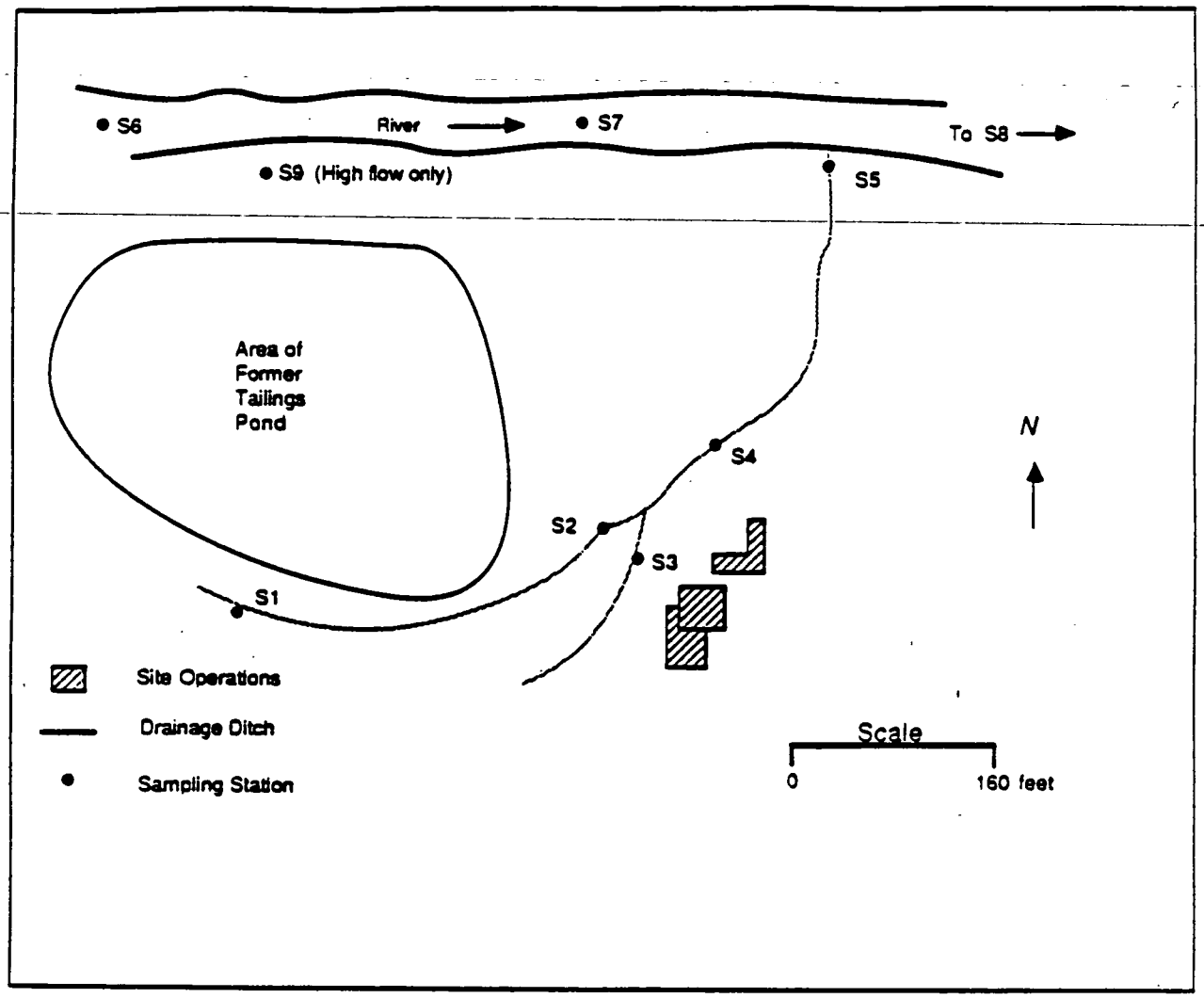

Figure 15-52. Sampling Station Locations for Surface Water Monitoring

Estimates of the distribution of metals between the dissolved and adsorbed phases for a range of partition coefficients (K_p) are shown in Table 15-16. For example, if $K_p = 10^4$ and the suspended solids concentration was 10 mg/l, 90 percent of the metal present would be in the dissolved phase. This information indicated that even though a metal (e.g., lead), was known to sorb strongly, a significant amount could be transported in the dissolved phase. Thus, both water and suspended solids should be analyzed for metals. The complete list of parameters selected for measurement in the Phase I investigation and the rationale for their selection are outlined in Table 15-17.

The sampling stations were selected to determine river quality up- and downstream of the site and to determine whether particulates with sorbed metals were deposited on the river banks or streambed. The sampling stations and the rationale for their selection are listed in Table 15-18. The station locations are shown in Figure 15-52. Because floods were considered to be one cause of contamination incidents, samples were to be collected under both high and low flow conditions.

Selected results of the surface water quality sampling program for spring conditions are given below:

Station	Dissolved Copper Concentration, µg/ℓ
S5 (mouth of ditch)	1110
S7 (upstream)	2.7
S8 (downstream)	4.0

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TABLE 15-16

RELATIONSHIP OF DISSOLVED AND SORBED PHASE POLLUTANT CONCENTRATIONS TO PARTITION COEFFICIENT AND SEDIMENT CONCENTRATION

K_p	SS (ppm)	C_W/C_T[a]	If C_T = 100 ppb		
			C_W =	X =	C_S =
10^0	1	1.0	100.	100.	0.0
	10	1.0	100.	100.	0.0
	100	1.0	100.	100.	0.0
	1000	1.0	100.	100.	0.0
	10,000	1.0	99.	99.	1.0
10^1	1	1.0	100.	1×10^3	0.0
	10	1.0	100.	1×10^3	0.0
	100	1.0	99.9	999.	0.1
	1000	1.0	99.0	990.	1.0
	10,000	0.9	90.9	909.	9.1
10^2	1	1.0	100.	1×10^4	0.0
	10	1.0	99.9	1×10^4	0.1
	100	1.0	99.0	9.9×10^3	1.0
	1000	0.9	90.9	9.1×10^3	9.1
	10000	0.5	50.	5×10^3	50.
10^3	1	1.0	99.9	1×10^5	0.1
	10	1.0	99.0	9.9×10^4	1.0
	100	0.9	90.9	9.1×10^4	9.1
	1000	0.5	50.	5×10^4	50.
	10000	0.1	9.1	9×10^3	90.9
10^4	1	1.0	99.0	9.9×10^5	1.0
	10	0.9	90.9	9.1×10^5	9.1
	100	0.5	50.	5×10^5	50.
	1000	0.1	9.1	9.1×10^4	90.9
	10,000	0.0	1.0	9.9×10^3	99.0

After Mills et al., 1985.

[a]The fraction dissolved (C_W/C_T) is calculated as follows:

$$\frac{C_W}{C_T} = \frac{1}{1 + K_p \times 5 \times 10^{-6}}$$

here K_p = partition coefficient, ℓ/kg
SS = suspended solids concentration, mg/ℓ

TABLE 15-17

PARAMETERS SELECTED FOR SURFACE WATER MONITORING PROGRAM

Parameters	Rationale
Metals - As, Cd, Cu, Pb, Zn	Determine extent of contamination
pH	Predict sorption behavior, metal solubility, and speciation
Dissolved Oxygen, Sulfide, Fe(II), Fe(III)	Determine redox conditions which influence behavior of metals, particularly the leaching of tailings
Alkalinity	A measure of how well buffered a water is; allows consideration of the likelihood of pH change
Total Dissolved Solids	Used as a water quality indicator and for QA/QC checks
Major Cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH^{+}_{4}) Major Anions ($C1^{-}$, SO_4^{2-}, NO_3^{-})	May identify other waste sources; can influence fate of trace metals
Suspended Solids	Predict the fraction of metal in water which is sorbed
Streamflow	Compute mass balances and assist in identifying sources of observed contamination

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TABLE 15-18

SELECTED SURFACE WATER MONITORING STATIONS AND RATIONALE

Station	Media	Rationale
Drainage ditch west of site (S1)	Water and sediments	Determine whether off-site drainage is significant source of contamination
Drainage ditches on site (S2 and S3)	Water and sediments	Identify on-site sources
Downstream of confluence of 2 ditches (S4)	Water and sediments	Provide information for checking mass balances from the two drainage ditches
Mouth of drainage ditch (S5)	Water, suspended sediment, bedload	Determine upstream water quality
River (S6, S7, and S9)	Water, suspended sediment, bedload	Determine upstream water quality
River (S8)	Water, suspended sediment, bedload	Determine quality downstream of site and provide data for mass balance

A mass balance was computed to determine how much of the apparent decrease from the ditch (S5) to the downstream river sampling point (S8) was due to dilution and how much could be attributed to other processes (e.g., sorption, precipitation). The concentration in the river considering dilution alone was predicted using the following mass balance equation:

$$C_R = \frac{C_u Q_u + C_w Q_w}{Q_u + Q_w}$$

where

C_R = downstream concentration of pollutant in river following mixing with ditch waters (S8), µg/l

C_w = concentration in ditch water (S5), µg/l

C_u = concentration in river above ditch (S7), µg/l

Q_w = discharge rate of ditch, ft^3/sec

Q_u = flow rate of river above ditch, ft^3/sec.

At the time of sampling, the flow in the ditch at station S5 was 1 cfs and the river flow at station S7 was 155 cfs. Using the above equation, the predicted river concentration for Cu was approximately 10 µg/l. (The observed concentration was 4 µg/l.) The observed decrease in concentration was primarily due to dilution, although other attenuation processes (e.g., sorption) were probably occurring. The expected sorbed concentration was estimated as follows:

$$X = K_p C$$

where

X	=	sorbed concentration, µg/kg
K_p	=	partition coefficient, l/kg
C	=	concentration of dissolved phase, µg/l.

Here, the sorbed concentration of Cu was estimated as 8×10^5 µg/kg (800 mg/kg).

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Case Discussion

This case illustrates the use of site-specific data and the use of information on the environmental fate of contaminants in the design of a surface water monitoring program. Site data are needed to locate waste sources and to determine the likely flow paths by which contaminants reach rivers. An understanding of the general behavior of the contaminants of interest and of the factors which influence their fate is helpful in determining where samples should be collected and what parameters, particularly master variables, should be measured. Collecting data on such parameters (e.g., pH, suspended solids) ensures that the necessary information is available to interpret the data.

CASE STUDY 28: USE OF BIOASSAYS AND BIOACCUMULATION TO ASSESS POTENTIAL BIOLOGICAL EFFECTS OF HAZARDOUS WASTE ON AQUATIC ECOSYSTEMS

Point Illustrated

- Measurements of toxicity (i.e., bioassays) and bioaccumulation can be used to assess the nature and extent of potential biological impacts in off-site areas.

Introduction

A study was conducted to determine whether leachate discharged into surface waters had adversely affected biota in a stream adjacent to a waste site and in a nearby lake. The components of the study included chemical analyses of the leachate, surface waters, sediments, and tissue samples; toxicity testing of the surface waters; and surveys of the structure and composition of the biological communities. Tissue analyses are important for determining contaminant bio-accumulation and assessing potential human exposure through consumption of aquatic organisms. Toxicity testing is important for determining potential lethal and sublethal effects of contaminant exposure on aquatic biota. Although ecological analysis of community structure and composition is also an important component of biomonitoring, it will not be discussed here since the focus is on the relationships between the leachate source, the distributions of contaminants near the waste site, and the toxic effects and bioaccumulation of the contaminants in the tissues of local fauna.

Site Description

The 5-acre facility is an industrial waste processing site which accepts wastes from nearby plastic manufacturing and electroplating industries. Liquid wastes are dewatered on site prior to removal to an off-site disposal area. The principal wastes processed at the facility include several organic compounds and metals.

The site contains a wastewater impoundment with numerous seeps and drainage channels that transport leachate into an adjacent river (Figure 15-53). The river flows from northeast to southwest, and is joined by a tributary stream before

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entering a nearby lake. The RFA indicated an oily sheen associated with a strong chemical odor on the surface of the stream below the treatment pond, and further reported numerous violations of the NPDES permit. Subsequent analyses of samples taken from the drainage channels and seeps flowing into the river showed high concentrations of organic and trace metal contaminants, principally bis(2-ethylhexyl) phthalate, ethylbenzene, phenol, copper, cadmium, and zinc.

Sampling Program

Six stations were sampled to assess possible toxicity and bioaccumulation of released substances (Figure 15-53). Station 6, located upstream of the release, was selected as a reference location for the stream. Station 17 was selected as a reference location for the lake because it is distant from the river mouth and because prevailing winds from the northwest direct the river discharge along the southeast shore of the lake away from the station. Stations 7, 15, and 18 were selected to determine the extent of toxic impacts on river and lake biota.

Water, sediments, and tissues of bottom-dwelling fishes (brown bullhead catfish, *Ictalurus nebulosus*) were collected at each station. Concentrations of bis(2-ethylhexyl) phthalate, ethylbenzene, phenol, copper, cadmium, and zinc were measured in each matrix. Analyses were conducted according to U.S. EPA guidelines for sediments, water, and tissues. Water quality variables (dissolved oxygen, temperature profiles, and alkalinity), total organic carbon in sediments, and lipid content of tissues were also measured.

Three independent bioassays were conducted on each water sample. The test species and endpoints used in the bioassays were those recommended in the U.S. EPA protocol for bioassessment of hazardous waste sites (Tetra Tech, 1983). Growth inhibition in the alga *Selanastrum capricornutum*, and mortality in the crustacean *Daphnia magna* were determined using U.S. EPA (1985) short-term methods for chronic toxicity testing. Inhibition of enzyme-mediated luminescence in the bacterium *Photobacterium phosphoreum* (i.e., the Microtox procedure) was measured according to the methods established by Bulich *et al*. (1981).

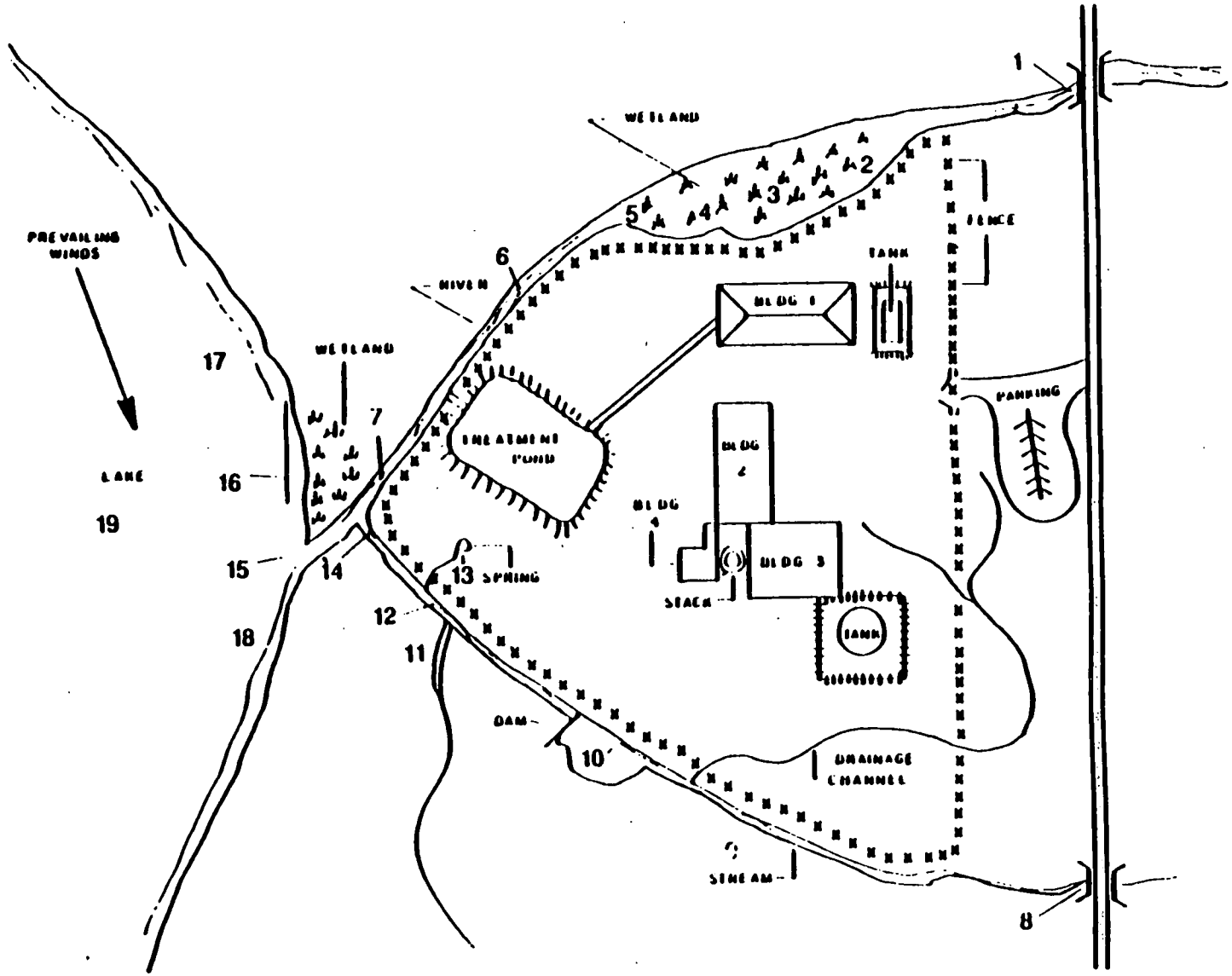

Figure 15-53. Site Plan and Water Sampling Locations

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Results

Results of the survey indicated that concentrations of organic contaminants in the surface waters were generally less than U.S. EPA water quality criteria, but that concentrations of inorganic contaminants generally exceeded water quality criteria at Stations 7, 15, and 18 (Table 15-19). In comparison with the reference stations, significant sediment contamination was evident at Stations 7, 15, and 18 for the three trace metals (Table 15-20). Tissue concentrations of organic substances exceeded detection limits for bis(2-ethylhexyl) phthalate at Stations 7 and 15, and for ethylbenzene at Station 7 (Table 15-21). However, trace metal concentrations in tissues were highly elevated at Stations 7 and 15, but only slightly elevated at Station 18.

The bioassay data showed a considerable range in sensitivity, with the algal bioassay being the most sensitive (Table 15-22). Consequently, the bioassay results were normalized to the least toxic of the reference stations (i.e., Station 6) to compensate for the wide range of sensitivity among the test species (Table 15-23). Overall, the bioassay results showed a high degree of agreement with contaminant concentrations in water and sediments (Figure 15-54, Table 15-19 and 15-20). Stations 7 and 15 showed highly toxic results, and Station 18 indicated moderate toxicity. Only the algal bioassay indicated significant, but low, toxicity at Station 17 (the lake reference station).

In summary, the results indicated that the organic contaminants were less of a problem than the trace metals in terms of bioaccumulation and potential toxicity. Most of the observed toxicity was attributed to trace metal contamination, which is consistent with the elevated concentrations of trace metals measured in the water, sediments, and tissues.

Case Discussion

This case study provides an example of a biomonitoring program designed to characterize the relationship between a contaminant source, contaminant concentrations in sediments and water, bioaccumulation in tissues, and receiving-water toxicity. It should be recognized that in many instances, the relationship

TABLE 15-19

MEAN CONCENTRATIONS (μg/ℓ) OF ORGANIC SUBSTANCES AND TRACE METALS IN LEACHATE AND SURFACE WATERS[a]

Chemical Class	Chemical	Station						Water Quality Criteria[b]	
		Seep L1	River 6	River 7	Lake 15	Lake 18	Lake 17	Acute	Chronic
Base Neutral	Bis (2-ethylhexyl) phthalate	600	2	11	10	1	2	940	3
Volatile	Ethylbenzene	100	1	1	<1	1	2	32,000	NA[c]
Acid Extractable	Phenol	1500	<1	18.37	<1	<1	<1	10,200	2560
Metals	Copper	4300	<1	489	56	26	2	18	12
	Zinc	35,000	17	4290	1100	37	35	320	47
	Cadmium	4800	<1	146	49	<1	<1	3.9	1.1

[a]River and lake alkalinity = 100 mg $CaCO_3$/L
[b]Trace metal criteria adjusted for alkalinity
[c]Not available for this substance

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TABLE 15-20

MEAN SEDIMENT CONCENTRATIONS (μg/kg DRY WT) OF ORGANIC SUBSTANCES AND TRACE METALS

Chemical Class	Chemical	Station					
		Seep L1	River 6	River 7	Lake 15	Lake 18	Lake 17
Base Neutral	Bis (2-ethylhexyl) phthalate	NA[a]	216	1188	1080	108	216
Volatile	Ethylbenzene	NA	10	34	20	14	8
Acid Extractable	Phenol	NA	<30	<30	<30	<30	<30
Metals	Copper	NA	3	1663	190	88	7
	Zinc	NA	11	28,314	7260	24	23
	Cadmium	NA	<0.1	19	6	<0.1	<0.1

[a]Not applicable (NA).

TABLE 15-21

MEAN LIVER TISSUE CONCENTRATIONS (µg/kg WET WT) OF ORGANIC SUBSTANCES AND TRACE METALS

Chemical Class	Chemical	Station					
		Seep L1	River 6	River 7	Lake 15	Lake 18	Lake 17
Base Neutral	Bis (2-ethylhexyl) phthalate	NA[a]	<25	95	86	<25	<25
Volatile	Ethylbenzene	NA	<5	9	<5	<5	<5
Acid Extractable	Phenol	NA	<30	<30	<30	<30	<30
Metals	Copper	NA	118	1600	750	237	180
	Zinc	NA	983	28,400	8500	2139	1420
	Cadmium	NA	115	1600	639	190	125

[a]Not applicable (NA).

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TABLE 15-22

MEAN LC_{50} AND EC_{50} VALUES (PERCENT DILUTION) FOR SURFACE-WATER BIOASSAYS[a]

Bioassay	Endpoint	Station					
		Seep L1	River 6	River 7	Lake 15	Lake 18	Lake 17
Algae	Growth inhibition (EC_{50}%)[d]	NA[b]	>100[c]	0.4	10.0	24.9	75.0
Daphnia	Mortality (LC_{50}%)[d]	NA	>100	3.3	18.5	100.0	90.0
Microtox	Decreased luminescence (EC_{50}%)[d]	NA	>100	5.6	15.0	43.4	>100

[a]Percent dilution required corresponding to a 50 percent response
[b]Not applicable (NA) because leachate toxicity was not tested
[c]Response of >100 indicates that samples were not toxic at all dilutions tested
[d]Percent dilution corresponding to 50 percent mortality

TABLE 15-23

RELATIVE TOXICITY OF SURFACE-WATER SAMPLES[a]

Bioassay	Endpoint	Station					
		Seep L1	River 6	River 7	Lake 15	Lake 18	Lake 17
Algae	Growth inhibition (EC_{50}%)	NA[b]	0.0	99.6	90.0	75.1	25.0
Daphnia	Mortality (LC_{50}%)	NA	0.0	96.7	81.5	0.0	10.0
Microtox	Decreased luminescence (EC_{50}%)[a]	NA	0.0	94.4	85.0	56.6	0.0

[a]Relative toxicity = 100 x [(Reference Station - Impacted Station)/Reference Station]
[b]Not applicable (NA) because leachate toxicity was not tested

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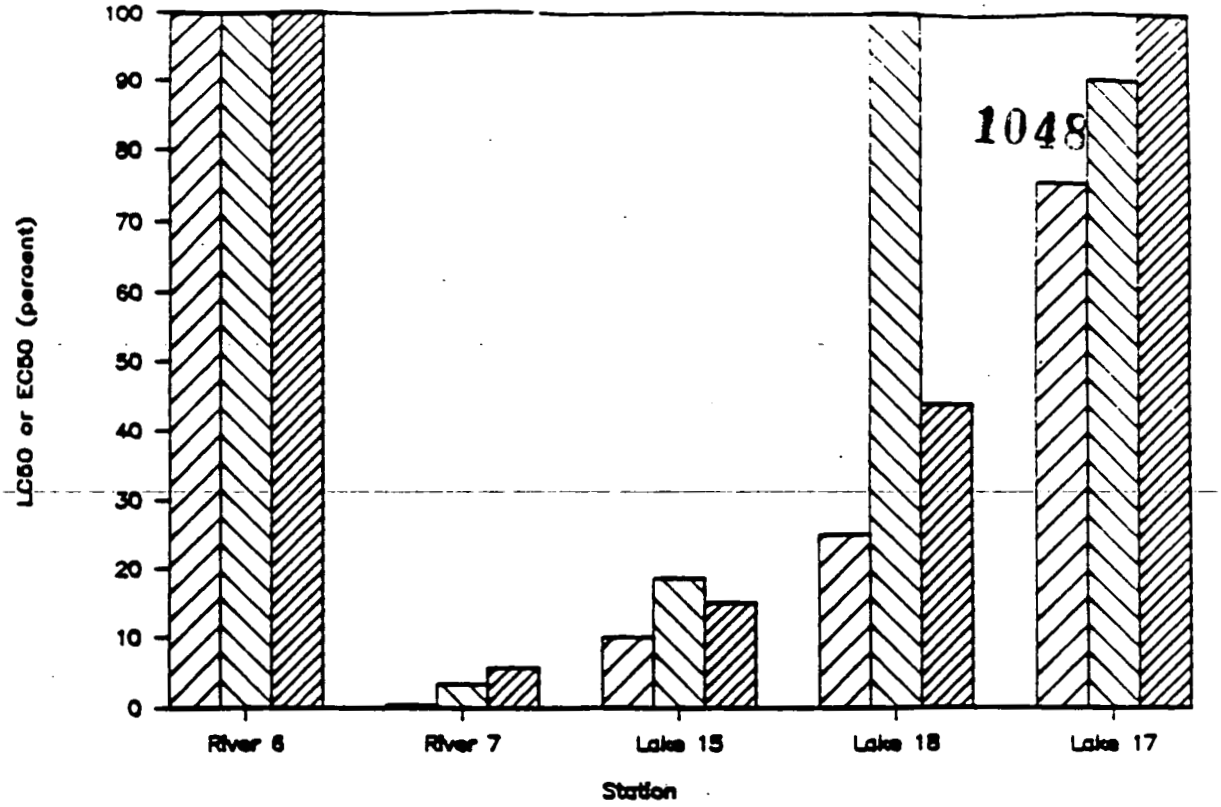

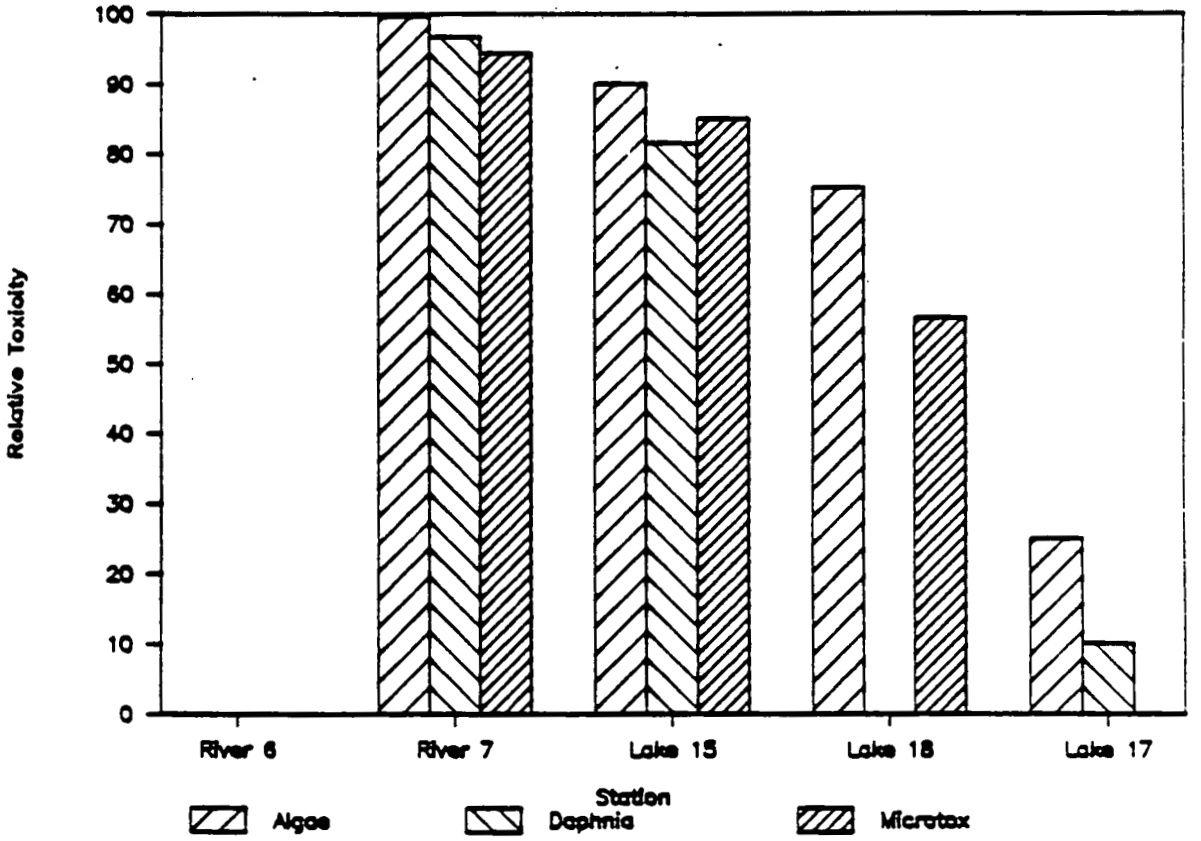

Figure 15-54. Bioassay Responses to Surface Water Samples

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between contaminant concentrations in the water and toxicity will not be as clear-cut as described in this example. Consideration of the chemical composition in leachate samples, mass balance calculations, and transport and fate mechanisms may indicate that sediments are the primary repository of contaminants. In such instances, sediment bioassays rather than receiving-water bioassays may be better suited for characterization of potential toxic effects on local fauna.

References

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Tetra Tech. 1983. Protocol for bioassessment of hazardous waste sites. EPA- 600/2-83-054. Lafayette, CA. 42 pp. + appendices.

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CASE STUDY 29: SAMPLING OF SEDIMENTS ASSOCIATED WITH SURFACE RUNOFF

Point Illustrated

- Contaminated sediments associated with surface runoff pathways (rivulets or channels) are indicative of the migration of chemicals via overland flow.

Introduction

This facility is a secondary lead smelting plant which began operation in 1976. The plant reclaims lead from materials such as waste automotive batteries, byproducts of lead weight manufacture, and wastewater sludges. Lead grid plates from salvaged batteries are temporarily stored on site in an open pile prior to being re-melted. It is therefore appropriate to conduct some form of runoff sampling to monitor migration of contaminants from the site via this route.

Facility Description

The facility covers approximately 2,000 ft^2 and is situated in an area primarily used for farming. A creek flows adjacent to the plant and drains into a major river 6 miles west of the site. Population is sparse with the nearest town 4 miles to the south. In the past, there have been four on-site impoundments in operation and two landfills. In addition, blast furnace slag, lead grid plates, and rubber chips from the recycled batteries have been stored in two on-site waste piles.

Sediment Sampling

Four sediment samples (020, 022, 025, and 027) were collected from surface runoff pathways and a creek which receives runoff from the site. Figure 15-55 shows the locations of the runoff pathways relative to the facility and the four sampling points. Additional sediment samples were collected from the creek at various points upstream and downstream of known overland leachate seeps and surface water runoff routes. The program design enabled comparison between

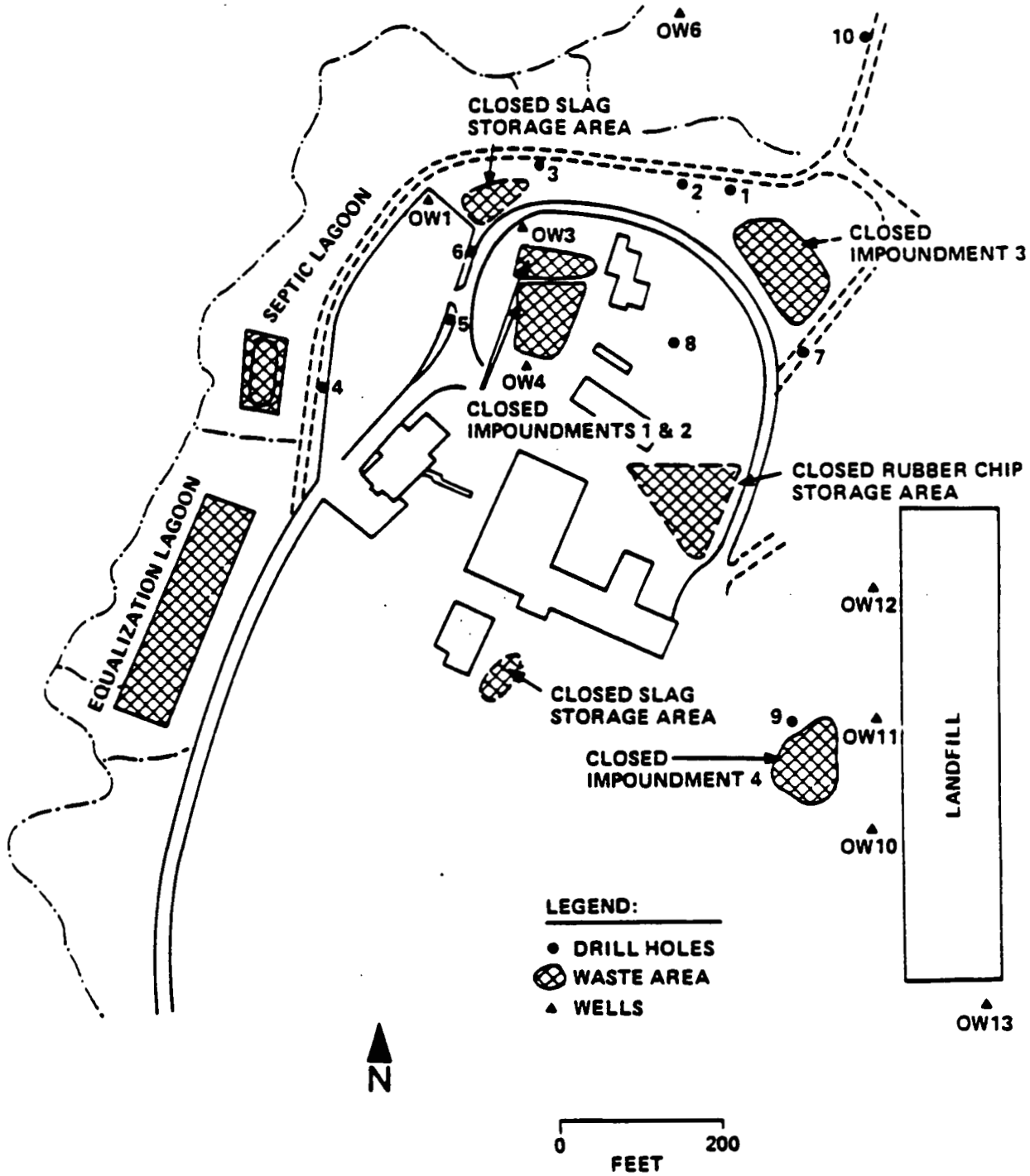

Figure 15-55. Surface Water and Sediment Sample Locations

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concentrations at different sections of the creek and background locations in relation to the runoff pathways.

Results

Table 15-24 presents the concentrations of lead and arsenic measured on the four surface runoff pathways and at location 029, which represents an upstream background concentration (Figure 15-55). It is clear that highly elevated levels of lead were detected in all four of the runoff pathway samples. The highest concentration of lead, 1,900 ppm, was detected in the western-most portion of the site. Runoff pathway sediment at the northern end of the facility, adjacent to the slag storage area, recorded 1,600 ppm of lead. Concentrations of this order represent a substantial source of sediment contamination.

TABLE 15-24

ARSENIC AND LEAD CONCENTRATIONS (PPM) IN RUNOFF SEDIMENT SAMPLES

	Sampling Location				
Contaminant	# 020	# 022	# 025	# 027	Background # 029
Arsenic	11.0	9.6	2.0	8.9	<0.1
Lead	1300	1900	1600	1700	11.0

Case Discussion

This case illustrates the importance of monitoring surface runoff pathways, because they can represent a major route of contaminant migration from a site, particularly for contaminants likely to be sorbed on or exist as fine particles. This type of monitoring is especially useful for units capable of generating overland flows. Such monitoring can establish the need for corrective measures (e.g., surface runon/runoff controls and/or some form of waste leachate collection system).

CASE STUDY 30: SAMPLING PROGRAM DESIGN FOR CHARACTERIZATION OF A WASTEWATER HOLDING IMPOUNDMENT

Points Illustrated

- Sampling programs should consider three-dimensional variation in contaminant distribution in an impoundment.
- Sampling programs should encompass active areas near inflows and outflows, and potentially stagnant areas in the corner of an impoundment.

Introduction

This study was conducted to assess whether an active liquid waste impoundment could be assumed to be of homogenous composition for the purpose of determining air emissions. This case shows the design of an appropriate sampling grid to establish the three-dimensional composition of the impoundment.

Facility Description

The unit being investigated in this study is a wastewater impoundment at a chemical manufacturing plant. The plant primarily produces nitrated aromatics and aromatic amines. Raw materials include benzene, toluene, nitric acid, and sulphuric acid. Wastewater from the chemical processing is discharged into the impoundment prior to being treated for release into a nearby water body. The impoundment has an approximate surface area of 3,750 m^2 and a depth of 3 m.

Sampling Program

For the most part, sampling involved the collection of grab samples using an extended reach man-lift-vehicle. The program was designed to collect samples at different locations and depths in the impoundment.

Sampling Locations and Procedures--

Sampling Grid - The wastewater impoundment was divided into 15 segments of equal area. Within this grid, eight sampling locations were selected which included all pertinent areas of the impoundment, such as active portions near the inflows and outflows, potential stagnant areas in the corners, and offshore points near the center line of the impoundment.

It was decided to take samples from four depths in the liquid layer and one from the bottom sediments at each of the eight locations. Figure 15-56 shows the impoundment schematic and sampling locations.

Liquid Sampling - A total of 32 liquid grab samples were taken. These were analyzed for the following parameters: all identifiable volatile organic compounds (VOCs) and semivolatile organic compounds (SVOCs) using gas chromatograph/mass spectroscopy; and selected VOCs and SVOCs by gas chromatography using a flame ionization detector.

Sediment/Sludge Sampling - The bottom layer was sampled using a Ponar grab sampler. The same analyses were performed on the eight sediment/sludge samples as on the liquid samples.

Meteorological Monitoring - The ambient meteorological conditions were monitored throughout the sampling period, including wind speed, wind direction, and air temperature. A video camera was also used to record the movement of surface scum on the impoundment.

Table 15-25 summarizes the sampling locations and analyses, including locations where QC data were collected.

Results

From the sampling program, it was discovered that approximately 99 percent of the organic compounds (by weight) were contained in the bottom sludge layer.

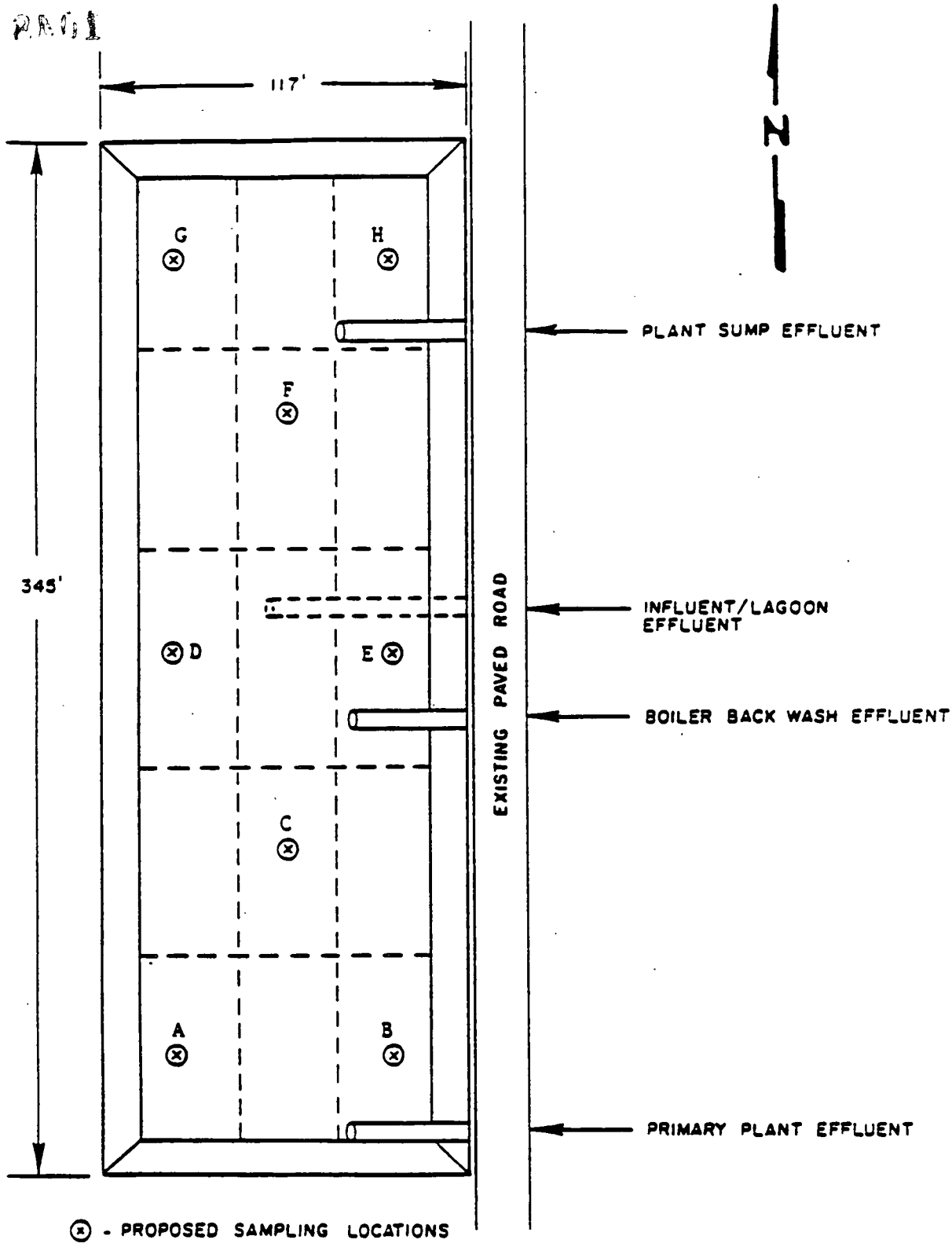

Figure 15-56. Schematic of Wastewater Holding Impoundment Showing Sampling Locations

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TABLE 15-25

SUMMARY OF SAMPLING AND ANALYSIS PROGRAM FOR WASTEWATER IMPOUNDMENT

Location	Depth (Feet)	Sample Analyses						
		GC/FID VOA	GC/MS VOA	TOC	POC	Onsite Parameters[a]	GC/FID SVOC	GC/MS SVOC
A-1	0-1	X	X	X	X	X	X	X
A-2	2	X				X	X	
A-3	4	X				X	X	
A-4	6	X				X	X	
A-5	Bottom Sediment	X	X	X		X	X	X
B-1	0-1	X	X	X	X	X	X	X
B-2	2	X				X	X	
B-3	4	X				X	X	
B-4	6	X				X	X	
B-5	Bottom Sediment	X	X	X		X	X	X
C-1	0-1	X	X	X	X	X	X	X
C-2	2	X				X	X	
C-3	4	X				X	X	
C-4	Bottom Sediment	X	X	X		X	X	X
D-1	0-1	X	X	X	X	X	X	X
D-2	2	X				X	X	
D-3	4	X				X	X	
D-4	6	X				X	X	
D-5	Bottom Sediment	X	X	X		X	X	X

a Includes pH, turbidity, specific conductance, and dissolved oxygen measurements.
X Indicates locations where QC samples were collected.

TABLE 15-25 (continued)

Location	Depth (Feet)	Sample Analyses						
		GC/FID VOA	GC/MS VOA	TOC	POC	Onsite Parameters[a]	GC/FID SVOC	GC/MS SVOC
E-1	0-1	X	X	X	X	X	X	X
E-2	2	X				X	X	
E-3	4	X				X	X	
E-4	6	X				X	X	
E-5	Bottom Sediment	X	X	X		X	X	X
F-1	0-1	X	X	X	X	X	X	X
F-2	2	X				X	X	
F-3	4	X				X	X	
F-4	6	X				X	X	
F-5	Bottom Sediment	X	X	X		X	X	X
G-1	0-1	X	X	X	X	X	X	X
G-2	2	X				X	X	
G-3	4	X				X	X	
G-4	6	X				X	X	
G-5	Bottom Sediment	X	X	X		X	X	X
H-1	0-1	X	X	X	X	X	X	X
H-2	2	X				X	X	
H-3	4	X				X	X	
H-4	6	X				X	X	
H-5	Bottom Sediment	X	X	X		X	X	X

a Includes pH, turbidity, specific conductance, and dissolved oxygen measurements.
X Indicates locations where QC samples were collected.

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Vertical and horizontal variation in the composition of the lagoon was apparent. The degree of horizontal variation was relatively small, but sample point "A" showed consideraby higher concentrations of 2,4-dinitrophenol than the other locations. This could have resulted from a recent discharge from the outflow at the southern end of the impoundment. Vertical variation in composition showed a general trend of increasing concentration with depth, but certain chemicals tended to have higher concentrations at mid-depth in the impoundment.

Case Discussion

This case provides an example of a sampling program at an areal source designed to yield accurate information for characterizing air emissions from the unit. The study illustrated the importance of characterizing the organic composition of the lagoon in three dimensions and considering variations resulting from inflow and outflow areas.

It should be mentioned that this study did not consider variation in the chemical composition of the impoundment with time. To obtain this information, it would be necessary to conduct subsequent sampling programs at different times. From this study, it is apparent that chemical composition varies both horizontally and vertically, and is likely to change depending on inflows and outflows of wastes. This sampling program is therefore limited to effectively characterizing composition at a single point in time.

CASE STUDY 31: USE OF DISPERSION ZONE CONCEPTS IN THE DESIGN OF A SURFACE WATER MONITORING PROGRAM

Point Illustrated

- Estimation of the dispersion zone of contaminants downstream of a release point can be used to help design a surface water monitoring program.

Introduction

When a contaminant is initially released to a body of water, the concentration of the contaminant will vary spatially until fully dispersed. In streams, the contaminant will disperse with the surrounding ambient water as the water moves downstream and will eventually become fully dispersed within the stream. Downstream of this point, the contaminant concentration will remain constant throughout the stream cross-section, assuming that streamflow is constant and that the contaminant is conservative (e.g., nondegradable). The area in which a contaminant's concentration will vary until fully dispersed, referred to here as the dispersion zone, should be considered when determining the number and location of sampling stations downstream of the release point.

Facility Description

A facility that processed zinc, copper and precious metals from ores operated along a stream for five years. The plant was closed after being cited for repeated fish kills, reportedly due to failures of a tailings pond dike. At present, the site is covered with tailings containing high concentrations of copper, zinc, cadmium, arsenic, and lead. There is no longer a tailings pond. This is the same facility described in Case Study 27.

Site Setting

The site is located on coarse colluvium (hill-slope deposits of weathered bedrock) and fine-grained alluvium. These deposits are typically 50 feet thick. Metamorphic rock (phyllite) underlies the unconsolidated materials. Ground water

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moves laterally in the gravel formations from the steep valley walls toward the stream.

The site is located about 400 feet from the stream. Two drainage ditches cross the lower portion of the site and merge prior to leaving the site. The ditch carries the combined flow and discharges directly into the stream (Figure 15-57). No other tributaries enter the stream within 2 miles of this location. Downstream of the release point, stream width and depth remain fairly constant at 45 and 3 feet, respectively. Mean stream velocity is 0.5 feet per second and channel slope is 0.0005 feet per foot.

Sampling Program

A surface water monitoring program was designed as part of a Phase I investigation to determine the extent of contamination in the stream. Existing data from previous sampling had shown high concentrations of metals in the drainage ditch sediments (e.g., 5,170 mg/kg Cu and 11,500 mg/kg Zn). Ground-water data from the plant's well showed concentrations of Cu (7 μg/ℓ) and Zn (54 μg/ℓ). The contribution of metals to the stream by ground-water discharge was considered to be relatively minor.

Based on a review of the plant history and the available water quality and sediment data, a monitoring program was designed. The potential pathways by which metals could reach the stream appeared to be direct discharge from the drainage ditch, discharge of contaminated ground water, and storm water runoff over the general facility area. Plant records indicated that typical flows in the drainage ditch at its confluence with the stream varied from 1 to 3 cubic feet per second (cfs) in the spring. During extreme flood conditions, the flow in the ditch exceeded 20 cfs. In the summer, flows in the drainage ditches at all locations were less than 0.5 cfs. Resuspension of contaminated sediments in the ditches during storm runoff appeared to be the most likely pathway for metals to reach the stream. The specific metals of concern were identified as As, Cd, Cu, Pb and Zn, based on the processes used at the plant and the composition of the ores which contained some arsenopyrites (with As, Cu), galena (Pb), and sphalerite (with Zn, Cd).

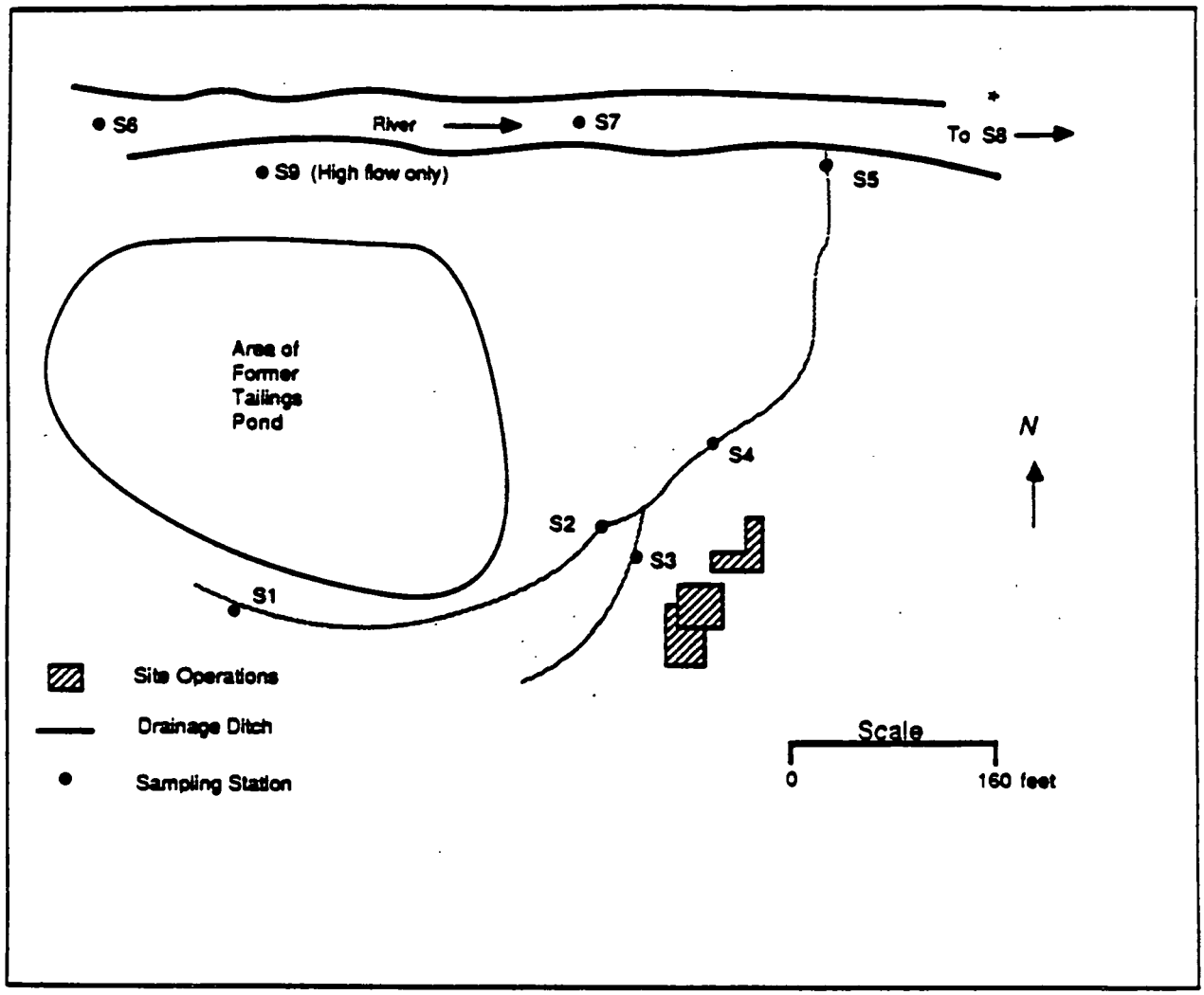

Figure 15-57. Sampling Station Locations for Surface Water Monitoring

- Located approximately 1030 feet downstream of the confluence of the ditch with the stream.

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The available soil and water quality data from previous sampling were reviewed to help determine the likely fate of the metals. The pH of soils in the area is about 6.5 and they contain about 0.5 percent organic matter by weight. Under such conditions, the metals, particularly Pb, would be expected to adsorb onto the soil particles. In the on-site tailings piles, the pH of core samples ranged between 3.3 and 4.9. Low soil pH values had been measured in sediments in the drainage ditch just downgradient of the tailings pile. The pH of the stream during the previous sampling was 6.9. The suspended solids concentration was 10 mg/l.

Estimates of the distribution of metals between the dissolved and adsorbed phases for a range of partition coefficients (K_p) are shown in Table 15-26. For example, if $K_p = 10^4$ and the suspended solids concentration was 10 mg/l, 90 percent (0.9) of the metal present would be in the dissolved phase. This information indicated that even though a metal (e.g., lead) was known to strongly sorb, a significant amount could still be transported in the dissolved phase. Thus, both water and suspended solids should be analyzed for metals. The complete list of parameters selected for measurement in the Phase I investigation and the rationale for their selection are outlined in Table 15-27.

The sampling stations were selected to determine stream water quality up- and downstream of the site and to determine whether particulates with sorbed metals were deposited on the stream banks or streambed. The sampling stations and the rationale for their selection are listed in Table 15-28. The station locations are shown in Figure 15-57. Because floods were considered a cause of contamination incidents, samples were to be collected under both high and low flow conditions.

The location of the downstream station (S8) was determined after estimating the stream length that may be required for complete dispersion of the contaminants. The following equation was used for this estimation:

$$DZ = \frac{0.4\,w2u}{0.6d\sqrt{gds}}$$

TABLE 15-26

RELATIONSHIP OF DISSOLVED AND SORBED PHASE CONTAMINANT CONCENTRATIONS TO PARTITION COEFFICIENT AND SEDIMENT CONCENTRATION

K_p	SS	C_W/C_T[a]
10^0	1	1.0
	10	1.0
	100	1.0
	1000	1.0
	10,000	1.0
10^1	1	1.0
	10	1.0
	100	1.0
	1000	1.0
	10,000	0.9
10^2	1	1.0
	10	1.0
	100	1.0
	1000	0.9
	10,000	0.5
10^3	1	1.0
	10	1.0
	100	0.9
	1000	0.5
	10,000	0.1
10^4	1	1.0
	10	0.9
	100	0.5
	1000	0.1
	10,000	0.0

After Mills et al., 1985.

[a]The fraction dissolved (C_W/C_T) is calculated as follows:

$$\frac{C_W}{C_T} = \frac{1}{1 + K_p \times 5 \times 10^{-6}}$$

where K_p = partition coefficient, ℓ/kg
SS = suspended solids concentration, mg/ℓ
C_w = Dissolved concentration
C_T = Total concentration

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TABLE 15-27

PARAMETERS SELECTED FOR SURFACE WATER MONITORING PROGRAM

Parameters	Rationale
Metals - As, Cd, Cu, Pb, Zn	Determine extent of contamination
pH	Predict sorption behavior, metal solubility, and speciation
Dissolved Oxygen, Sulfide, Fe(II), Fe(III)	Determine redox conditions which influence behavior of metals, particularly the leaching of tailings
Alkalinity	A measure of how well buffered a water is, allows consideration of the likelihood of pH change
Total Dissolved Solids	Used as a water quality indicator and for QA/QC checks
Major Cations (Ca^{+2}, Mg^{+2}, Na^{+}, K^{+}, NH_4^{+}) and Major Anions (Cl^{-}, SO_4^{-2}, NO_3^{-})	May identify other waste sources, can influence fate of trace metals
Suspended Solids	Predict the fraction of metal in water which is sorbed
Streamflow	Compute mass balances and assist in identifying sources of observed contamination

TABLE 15-28

SELECTED SURFACE WATER MONITORING STATIONS AND SELECTION RATIONALE

Station	Media	Rationale
Drainage ditch west of site (S1)	Water and sediments	Determine whether off-site drainage is significant source of contamination
Drainage ditches on site (S2 and S3)	Water and sediments	Identify on-site sources
Downstream of confluence of two ditches (S4)	Water and sediments	Provide information for checking mass balances from the two drainage ditches
Mouth of drainage ditch (S5)	Water, suspended sediment, bedload	Determine quality of direct discharge to stream
Stream (S6, S7 and S9)	Water, suspended sediment, bedload	Determine upstream water quality
Stream (S8)	Water, suspended sediment, bedload	Determine quality downstream of site following complete dispersion and provide data for mass balance

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where:

DZ	=	dispersion zone length, ft
w	=	width of the water body, ft (45 ft)
u	=	stream velocity, ft/sec (0.5 ft/sec)
d	=	stream depth, ft (3 ft)
s	=	slope (gradient) of stream channel, ft/ft (0.0005)
g	=	accerleration due to gravity (32 ft/sec^2).

Using the above equation, the estimated stream length required for complete contaminant dispersion is 1030 feet. This can serve as an approximate distance downstream of the release point at which a sampling station should be located.

Case Discussion

This case illustrates the use of contaminant dispersion zones in the design of a surface water monitoring program. In this example, the data indicate that approximately 1030 feet of flow within the described stream channel is required before a contaminant will become fully dispersed. A downstream station should therefore be located at or below this dispersion zone to fully characterize the extent of the release. An adequate number of sampling stations should also be located upstream of this point.

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