LMS/WEL/S02589

Baseline Concentrations of the Chemical Plant Groundwater Operable Unit Monitored Natural Attenuation Network at the Weldon Spring, Missouri, Site

July 2008

U.S. Department of Energy

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Appendix

Appendix A. Contaminant Distributions—2002 Data

Acronyms and Abbreviations

1,3-DNB	1,3-dinitrobenzene
2,4-DNT	2,4-dinitrotoluene
2,6-DNT	2,6-dinitrotoluene
1,3,5-TNB	1,3,5-trinitrobenzene
2,4,6-TNT	2,4,6-trinitrotoluene
ANL	Argonne National Laboratory, Environmental Assessment Division
ARAR	applicable or relevant and appropriate requirement
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
cm/s	centimeters per second
COC	contaminant of concern
DA	U.S. Department of the Army
DOE	U.S. Department of Energy
DOE-LM	U.S. Department of Energy, Office of Legacy Management
ft	feet
gpm	gallons per minute
GWOU	Groundwater Operable Unit
ICO	in situ chemical oxidation
IRA	interim remedial action
K_d	soil-water distribution coefficient
LM	Legacy Management
m	meters
MCL	maximum contaminant level
µg/L	micrograms per liter
MDNR	Missouri Department of Natural Resources
mg/L	milligrams per liter
MNA	monitored natural attenuation
NB	nitrobenzene
N	nitrogen
pCi/L	picocuries per liter
R	retardation factor
RAO	remedial action objective
RD/RA	remedial design/remedial action
RI	remedial investigation
ROD	Record of Decision
TCE	trichloroethylene
USGS	U.S. Geological Survey
WSTA	Weldon Spring Training Area

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1.0 Introduction

1.1 Purpose of the Report

The monitored natural attenuation (MNA) remedy selected for the Groundwater Operable Unit (GWOU) at the Weldon Spring Chemical Plant was implemented in July 2004 with the sampling of the network of groundwater wells and springs identified in the remedial design/remedial action (RD/RA) work plan (DOE 2004b). Baseline monitoring of the MNA groundwater and spring locations was performed for a 2-year period to obtain a comprehensive set of data for future evaluation.

The primary objective of this report was to evaluate monitoring data collected from July 2004 through May 2006 to establish baseline concentrations for the contaminants of concern (COCs) for each well and spring in the MNA network. These baseline concentrations were used to reevaluate the remediation timeframes and assess the long-term monitoring program.

A summary is presented herein of the modeling that was performed in 2003 to estimate times that would be involved in achieving aquifer remediation at the GWOU (DOE 2003) via natural attenuation. Inspection of COC concentration data collected since that time indicates that changes in contaminant levels have been relatively minor, for the most part, and that changes in plume configuration have also been minor. Consequently, the modeling calculations are not revised in this report, and the previously computed remediation times are believed to be applicable to current conditions.

Moreover, this report presents the methodology for review and evaluation of future MNA data. Timeframes for program reevaluation are also discussed.

1.2 Scope of the Report

A brief description and history of the site and the GWOU in particular is provided as background information in Section 2.0. In addition, because much of what has been observed thus far regarding the attenuation of groundwater contamination at the Weldon Spring Chemical Plant is affected not only by residual contamination but also by the various hydrological processes occurring in the chemical plant area, descriptions of those processes, how they tend to vary in both space and time, and the uncertainties associated with them are included in Section 2.0. This section provides summaries of two field studies conducted at the site before the selection and implementation of the MNA remedy. Estimates of MNA timeframes performed in 2003 (DOE 2003) to support remedy selections are also reproduced in this section. Collectively, this background information should facilitate an understanding of future observations regarding natural attenuation of the COCs in the GWOU at the Weldon Spring Site.

Section 3.0 presents the data collected during the baseline period, focusing on the temporal behavior of COC concentrations in wells and springs.

Section 4.0 presents a reevaluation of the MNA timeframes using the baseline data and contaminant distributions discussed in Section 3.0.

Section 5.0 provides the methodology for review and evaluation of future MNA data.

Section 6.0 presents an assessment of the current MNA monitoring program and provides changes for future monitoring.

Section 7.0 presents a report summary and conclusions from the baseline monitoring.

2.0 Background Information Relevant to the GWOU MNA Remedy

The Weldon Spring Site is located in St. Charles County, Missouri, about 30 miles (48 kilometers) west of St. Louis (Figure 2−1). The site consists of two geographically distinct DOE-owned properties: the Weldon Spring Chemical Plant (chemical plant area) and the Weldon Spring Quarry (quarry). The chemical plant is located about 2 miles (2.3 kilometers) southwest of the junction of Missouri State Route 94 and U.S. Highway 40/61 (Figure 2−1 and Figure 2–2). The quarry is about 4 miles southwest of the chemical plant. Both sites are accessible from Missouri State Route 94. The areas encompassed by the chemical plant area and the quarry are about 226 and 9 acres (91 and 3.6 hectares), respectively.

The U.S. Army owns about 1,655 acres (670 hectares) west of the chemical plant area (Figure 2−2) that is currently controlled by the 89th Regional Readiness Command and is used as a training area (Weldon Spring Training Area [WSTA]) for Army troops. The August A. Busch Memorial Conservation Area, located north of the chemical plant, encompasses about 6,987 acres (2,828 hectares) of actively managed grassland and forest. The Weldon Spring Conservation Area consists of about 7,356 acres (2,977 hectares) of primarily forested land located south and east of the chemical plant. Both conservation areas are actively managed for fish and wildlife production and are used annually by more than 1,200,000 visitors. Additional properties located near the chemical plant include Francis Howell High School, Weldon Spring Heights, and the Missouri Research Park.

2.1 Site Hydrogeology

The chemical plant site is in a physiographic transitional area between the Dissected Till Plains of the Central Lowlands province to the north and the Salem Plateau of the Ozark Plateaus province to the south. Subsurface flow and transport of concern in the chemical plant area occurs within two major geologic units: unconsolidated surficial materials and carbonate bedrock. The unconsolidated surficial materials are collectively referred to as overburden, which tends to consist of clay-rich, mostly glacially derived units that are generally unsaturated (Figure 2–3). Included in the overburden category are topsoil and fill located at the ground surface and residuum consisting of highly weathered limestone bedrock at the base of the overburden column. Local thicknesses of the unconsolidated materials that constitute overburden range from 20 to 50 feet (ft) (6.1 meters [m] to 15.3 m) (DOE and DA 1997).

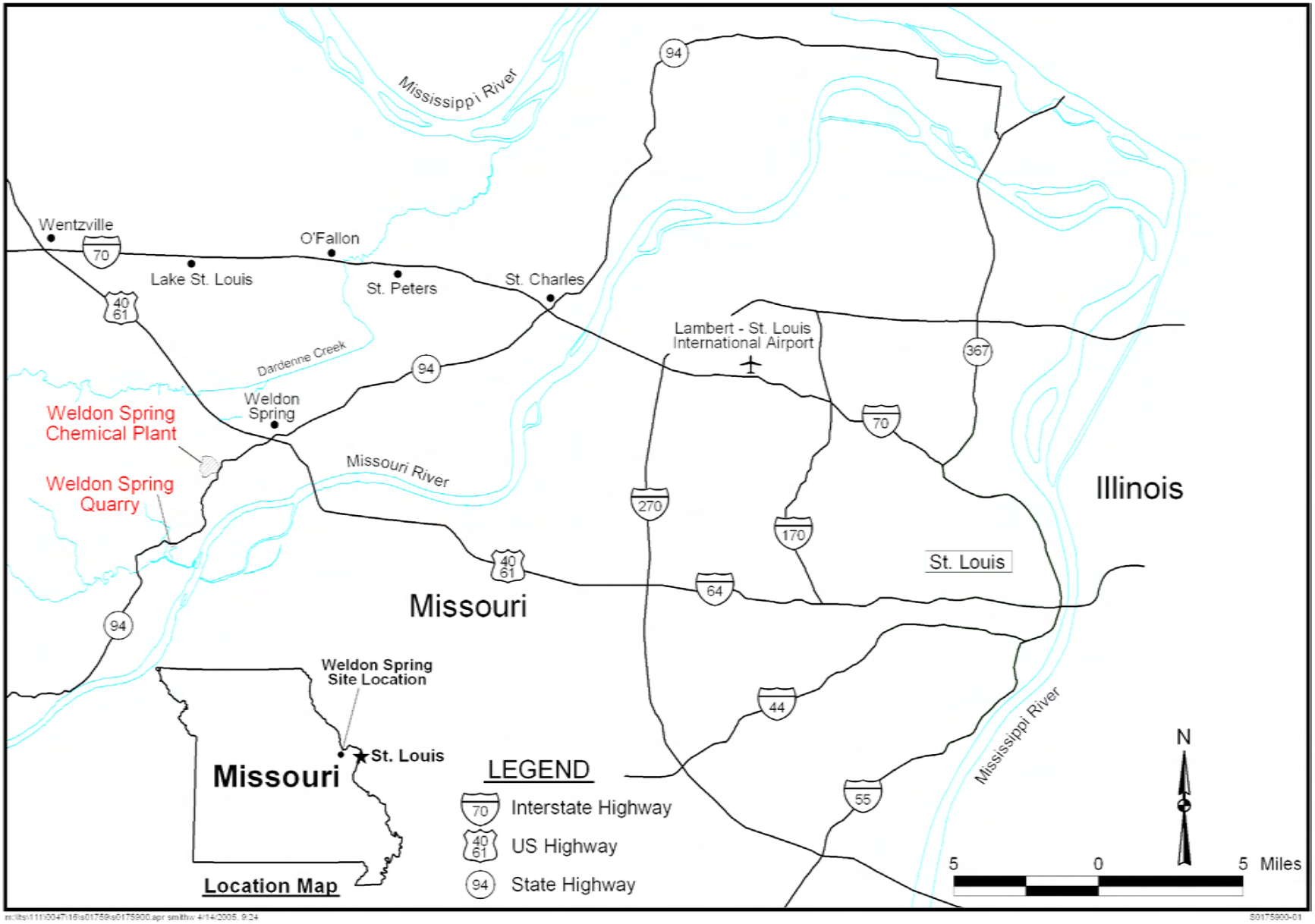

Figure 2–1. Location of the Weldon Spring Site

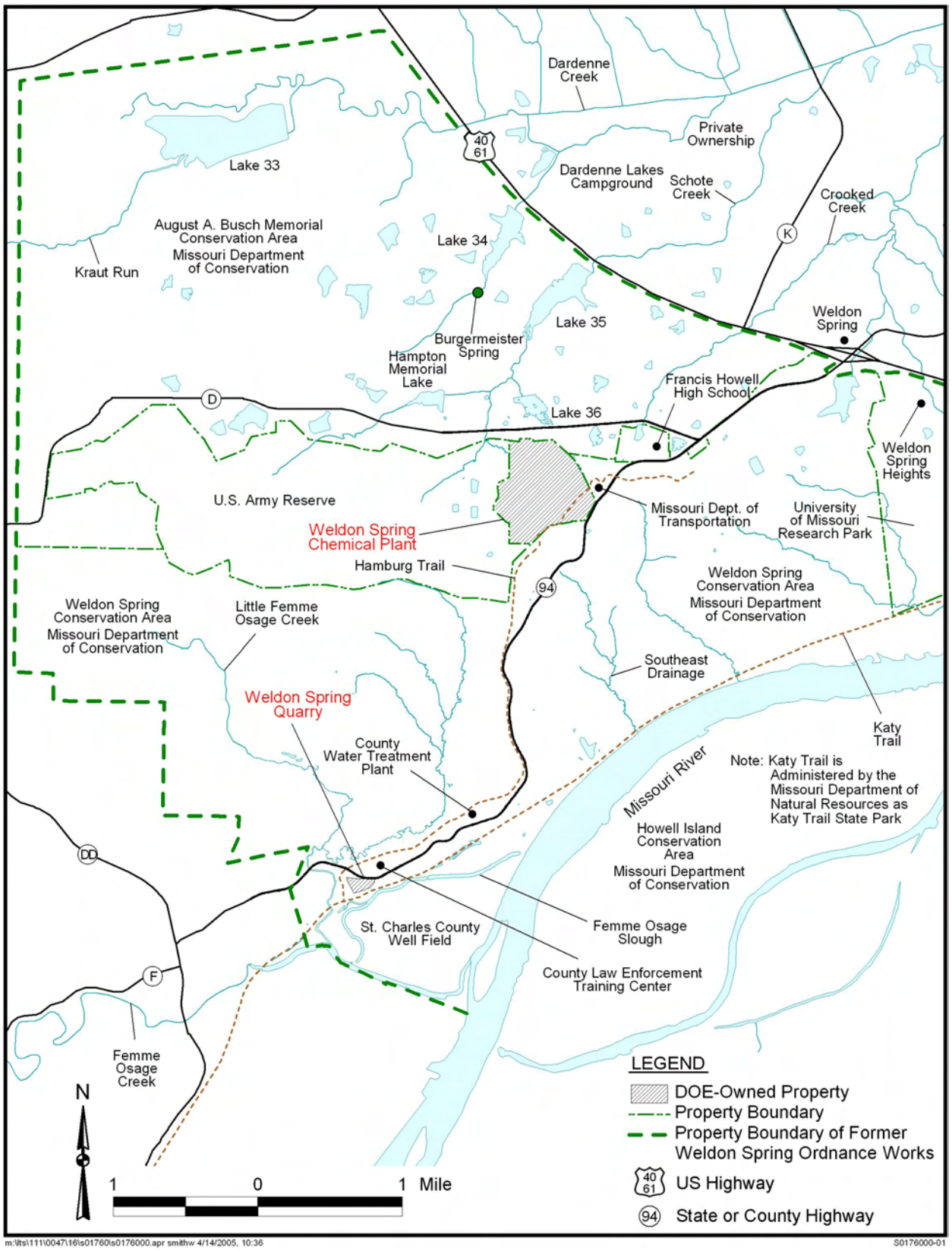

Figure 2–2. Vicinity Map of the Weldon Spring Site

System	Series	Stratigraphic Unit	Typical Thickness (ft)[a]	Physical Characteristics	Hydrostratigraphic Unit
Quaternary	Holocene	Alluvium	0–120	Gravelly, silty loam	Alluvial aquifer
	Pleistocene	Loess and glacial drift[b]	10–60	Silty clay, gravelly clay, silty loam, or loam over residuum from weathered bedrock	Locally a leaky confining unit[c]
Mississippian	Meramecian	Salem Formation[c]	0–15	Limestone, limey dolomite, finely to coarsely crystalline, massively bedded, and thin bedded shale	
		Warsaw Formation[c]	0–80	Shale and thin to medium bedded finely crystalline limestone with interbedded chert	
	Osagean	Burlington-Keokuk Limestone	100–200	Cherty limestone, very fine to very coarsely crystalline, fossiliferous, thickly bedded to massive	Shallow aquifer system
		Fern Glen Limestone	45–70	Cherty limestone, dolomitic in part, very fine to very coarsely crystalline, medium to thickly bedded	
	Kinderhookian	Chouteau Limestone	20–50	Dolomitic argillaceous limestone, finely crystalline, thin to medium bedded	Upper leaky confining unit
Devonian	Upper	Sulphur Springs Group Bushberg Sandstone[d]	40–55	Quartz arenite, fine to medium grained, friable	
		Lower part of Sulphur Springs Group undifferentiated		Calcareous siltstone, sandstone, oolitic limestone, and hard carbonaceous shale	
Ordovician	Cincinnatian	Maquoketa Shale[e]	0–30	Calcareous to dolomitic silty shale and mudstone, thinly laminated to massive	
	Champlainian	Kimmswick Limestone	70–100	Limestone, coarsely crystalline, medium to thickly bedded, fossiliferous and cherty near base	Middle aquifer system
		Decorah Group	30–60	Shale with thin interbeds of very finely crystalline limestone	Lower confining unit
		Plattin Limestone	100–130	Dolomitic limestone, very finely crystalline, fossiliferous, thinly bedded	
		Joachim Dolomite	80–105	Interbedded very finely crystalline, thinly bedded dolomite, limestone, and shale; sandy at base	
		St. Peter Sandstone	120–150	Quartz arenite, fine to medium grained, massive	Deep aquifer system
	Canadian	Powell Dolomite	50–60	Sandy dolomite, medium to finely crystalline, minor chert and shale	
		Cotter Dolomite	200–250	Argillaceous, cherty dolomite, fine to medium crystalline, interbedded with shale	
		Jefferson City Dolomite	160–180	Dolomite, fine to medium crystalline	
		Roubidoux Formation	150–170	Dolomitic sandstone	
		Gasconade Dolomite	250	Cherty dolomite and arenaceous dolomite (Gunter Member)	
Cambrian	Upper	Eminence Dolomite	200	Dolomite, medium to coarsely crystalline, medium bedded to massive	
		Potosi Dolomite	100	Dolomite, fine to medium crystalline, thickly bedded to massive; drusy quartz common	

Figure 2–3. Generalized Stratigraphy and Hydrostratigraphy of the Weldon Spring Site

The aquifer of concern beneath the former chemical plant, raffinate pits, and vicinity properties is the shallow bedrock aquifer located directly below the overburden. This shallow aquifer consists of Mississippian-age Burlington-Keokuk Limestone (the uppermost bedrock unit) and the underlying Fern Glen Formation (Figure 2–3). The Burlington-Keokuk Limestone, which ranges locally in thickness from 40 to 180 ft (12.2 to 54.5 m), is generally described as containing a shallow weathered zone and an underlying unweathered zone. The weathered portion of this formation is highly fractured and exhibits solution voids and enlarged fractures. These features may also be found on a limited scale in the unweathered zone of the Burlington-Keokuk Limestone, which is thinly bedded in some locales and massively bedded in others. Fracture densities are significantly less in the unweathered zone than in the weathered zone. Aquifer properties vary in space in response to changes in fracture spacing, solution voids, and pre-glacial weathering. In many locations where weathering is more significant than others, structural troughs referred to as paleochannels occur along the bedrock/overburden interface.

Regional groundwater flow in deep aquifers at the Weldon Spring Site is toward the east-northeast. Groundwater flow in the shallow aquifer is controlled largely by the bedrock topography. The southernmost portion of the site sits on a shallow groundwater divide, from which some groundwater flows north toward Dardenne Creek and then ultimately to the Mississippi River, and the remainder flows south to the Missouri River. Much of the groundwater movement in the shallow aquifer is by relatively diffuse flow within continuous porous media, but localized zones of discrete fracture-controlled flow are also present. The areas of greatest permeability tend to be associated with the trough-like paleochannels that represent bedrock lows.

Springs, a common feature in carbonate terrains, are present in the vicinity of the chemical plant area. Some of the springs are south of the plant in the Southeast Drainage. Several other springs are located to the north of the plant and adjacent to an unnamed tributary to Dardenne Creek (Figure 2–2). One of these, Burgermeister Spring, has been shown to have a relatively quick hydraulic connection to groundwater in the plant area as a result of preferential flow through fractured and weathered carbonate rock. Many reaches of the creeks north of the chemical plant appear to gain in flow due to groundwater discharge to them, and the springs provide an additional source of stream-flow augmentation. However, as mentioned in Section 2.0, not all stream reaches are gaining; losses of surface water to the subsurface have been observed along some local watercourses.

A surface drainage divide approximately aligned with the south boundary of the chemical plant area causes runoff from the area to flow into separate river systems. Surface water in the southernmost portion of the site flows south toward the Missouri River, primarily within the Southeast Drainage (Figure 2–2). Runoff from the central and northern portions of the plant area and to the west of the plant area flows toward Dardenne Creek and its tributaries, the largest of which is Schote Creek (Figure 2–2). These creeks, which can have both gaining and losing segments, flow east-northeastward toward the Mississippi River.

Under natural background conditions, groundwater recharge at the chemical plant area occurs primarily as infiltration of precipitation through the overburden and from losses of surface water runoff to the subsurface. In the past, recharge has also resulted from the infiltration of water stored in surface water impoundments, such as wastewater in former raffinate pits 1 through 4

and runoff detained in basins constructed near the northwest corner (Ash Pond) and the eastern boundary (Frog Pond) of the chemical plant area (Figure 2–4). The relatively high hydraulic heads associated with the pits and basins likely caused greater downward seepage of infiltrating water through overburden to fractured limestone than would have occurred due to infiltration of precipitation alone. Groundwater mounding occurred in the shallow aquifer beneath the pits and the basins in response to enhanced recharge in these areas.

The vast majority of groundwater within the shallow aquifer beneath the chemical plant area flows horizontally to the north, and a minor amount of vertical groundwater movement to deeper formations is also thought to occur (Kleeschulte and Imes 1994). Most groundwater flow in the limestone occurs in the direction of greatest permeability, which is principally aligned with bedding planes and fracture solution features that tend to extend greater distances horizontally than they do vertically (DOE and DA 1997). The residuum found near the bedrock/overburden contact has, in some cases, been identified as being more permeable than the overlying clayey materials and the underlying weathered bedrock zone due to the presence of relic chert beds, gravels, and heavily weathered limestone within it. Preferential horizontal flow can take place within this zone when saturated. Additional areas of preferential horizontal flow are associated with paleochannels that generally begin in the plant area and then course northward toward Burgermeister and other springs and tributaries to Dardenne Creek. Discharge to both springs and tributaries to Dardenne Creek causes upward gradients to be observed in the shallow aquifer in the vicinity of the springs and tributaries.

A north-to-south cross-sectional depiction of the conceptual model of groundwater flow at the Weldon Spring Site is presented in Figure 2–5. This graphic illustrates the predominantly horizontal shallow groundwater flow that takes place both to the north and south of the groundwater divide that is approximately aligned with the south boundary of the chemical plant area and the subsequent discharge of this groundwater to springs and surface water bodies.

An areal depiction of preferential flow zones in and near the chemical plant area, as surmised from hydrogeologic characterization of the region, is shown in Figure 2–6. Such zones are composed of the paleochannels in the weathered zone of the Burlington-Keokuk Limestone, several of which appear to originate beneath the chemical plant area and then extend northward toward Schote and Dardenne creeks. A map showing the groundwater potentiometric surface in the weathered zone of the Burlington-Keokuk Formation (Figure 2−7) illustrates the generally northward trending gradients that control shallow groundwater migration from the groundwater divide along the south boundary of the site. Troughs in the groundwater surface typically coincide with these paleochannel features.

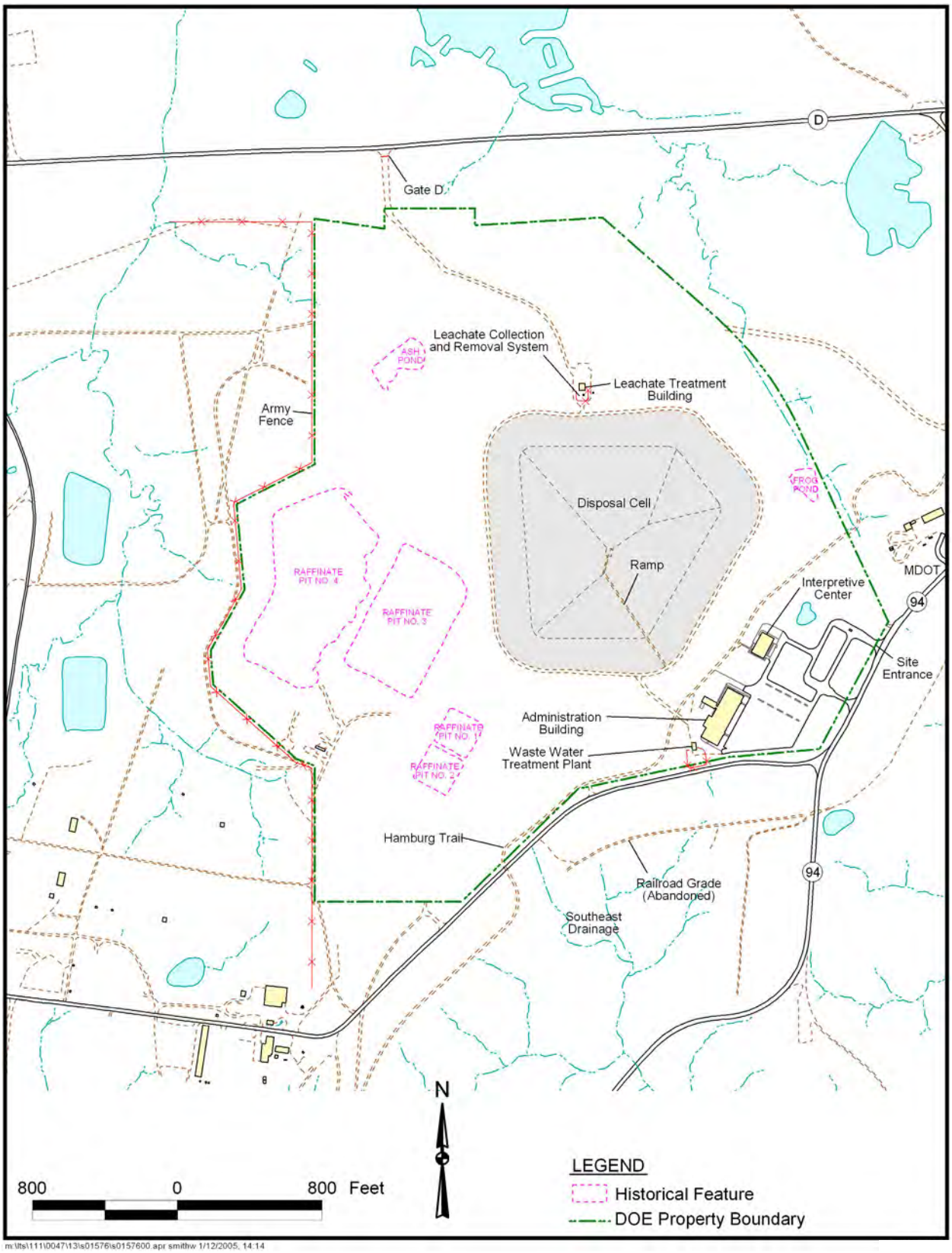

Figure 2–4. Layout of the Weldon Spring Chemical Plant

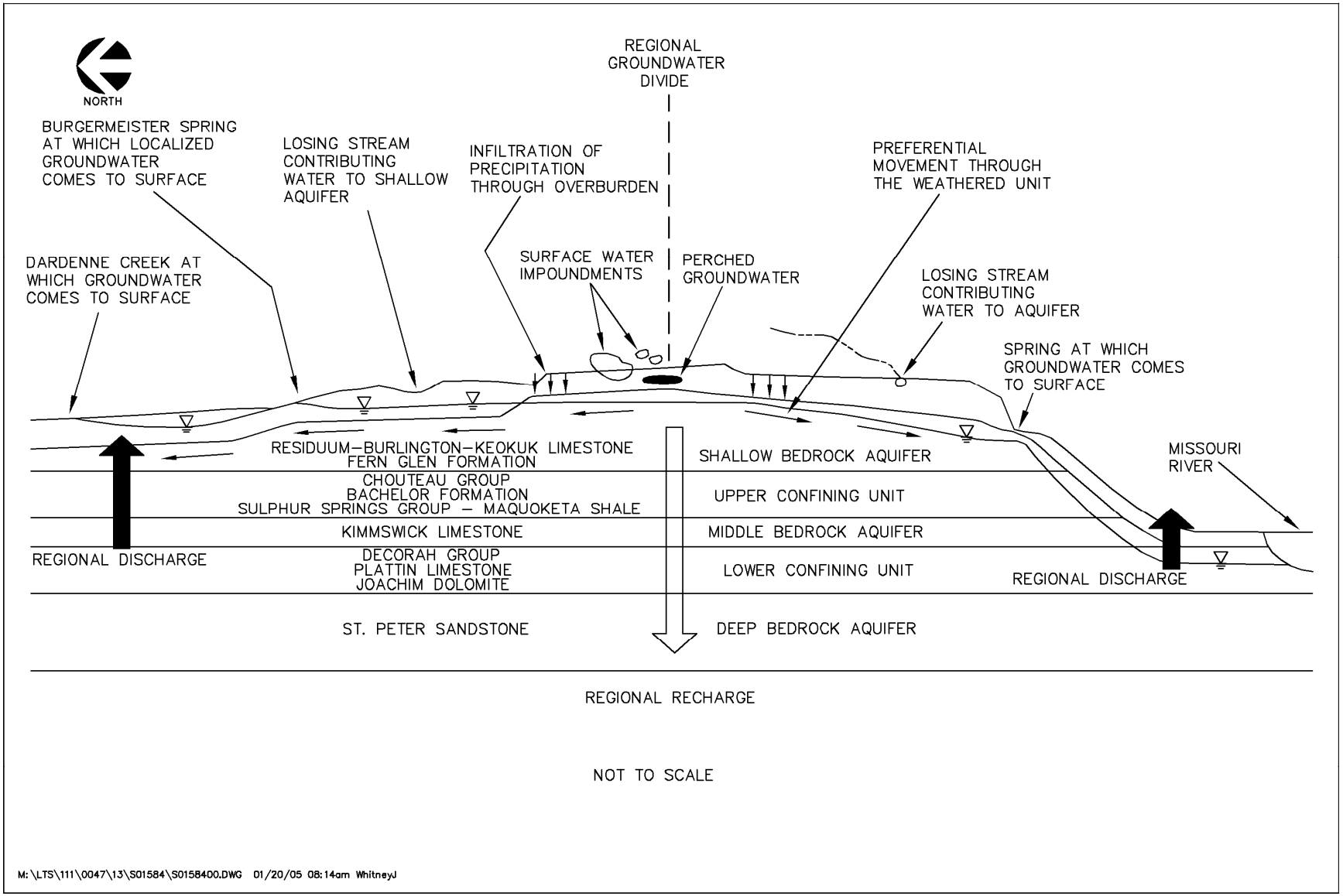

Figure 2–5. Hydrogeologic Conceptual Model for the Weldon Spring Site

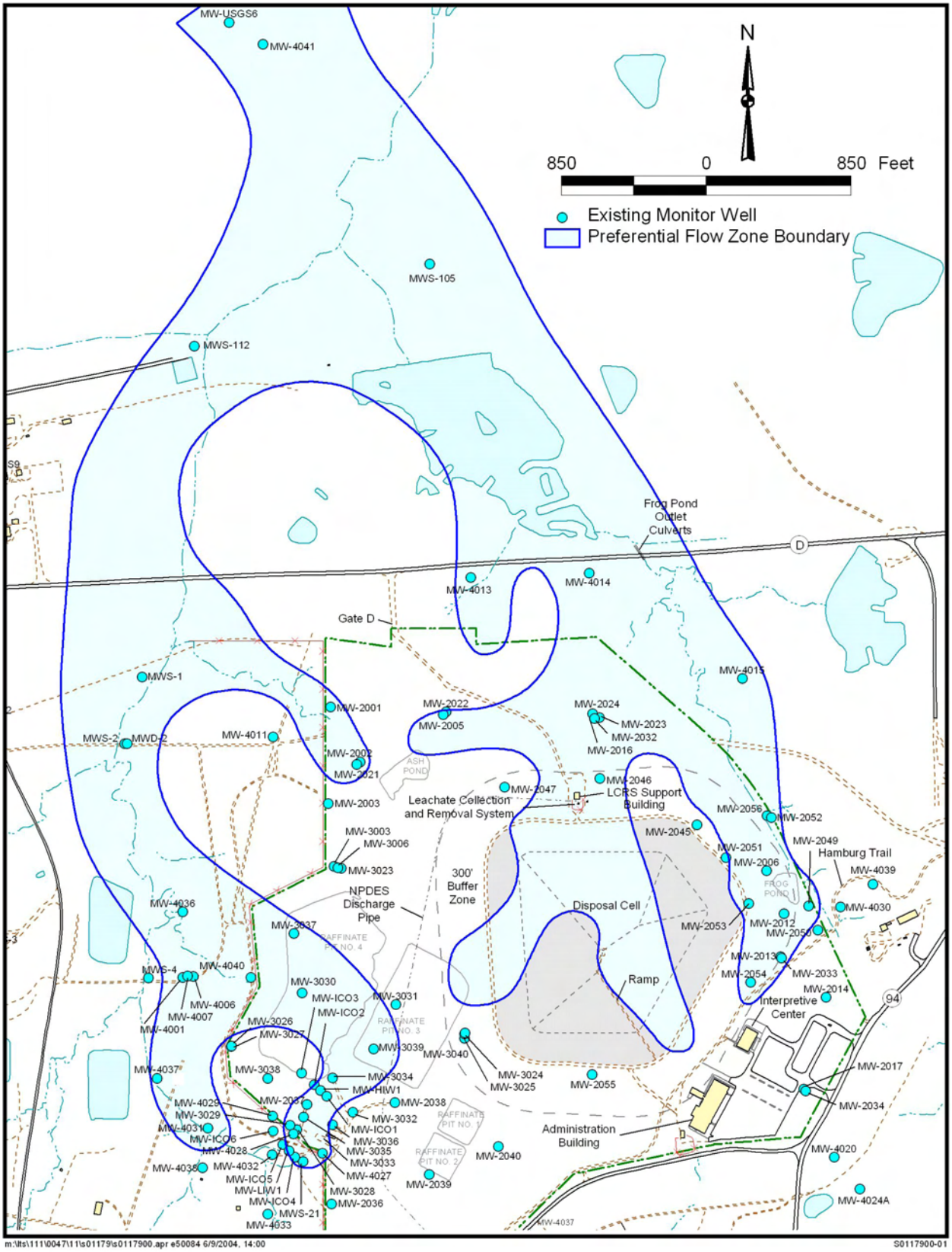

Figure 2–6. Preferential Flow Paths in the Burlington-Keokuk Limestone at the Chemical Plant Area

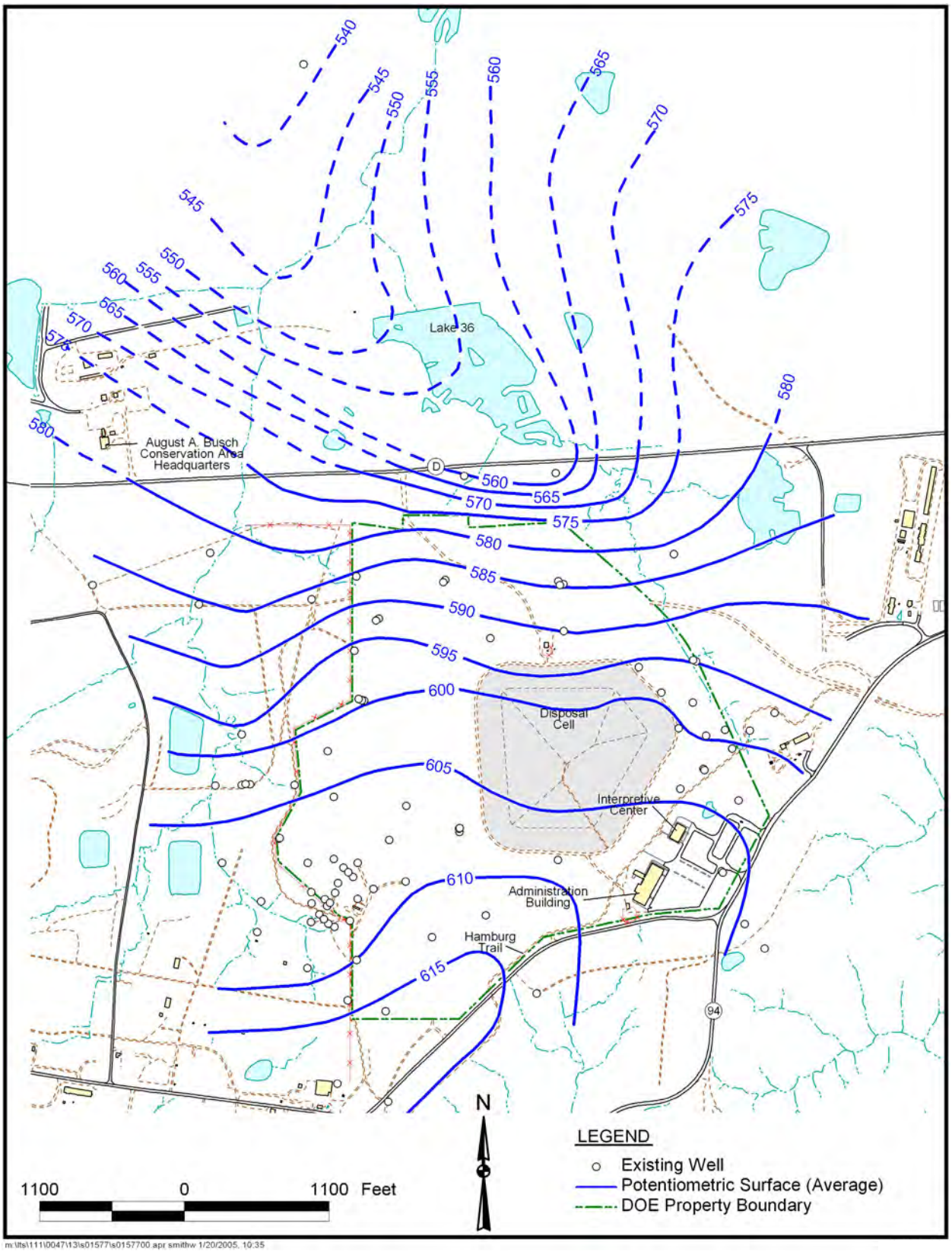

Figure 2–7. Potentiometric Surface of the Shallow Aquifer (Weathered Zone) (groundwater elevations in units of feet above mean sea level)

The foregoing descriptions of the hydrogeology of the chemical plant area indicate that the shallow groundwater system is complex. This complexity will likely have effects on observations made for the purpose of tracking MNA progress over the next several years. For example, because the hydraulic properties of the shallow aquifer can vary significantly both horizontally and vertically, it is likely that some portions of the shallow subsurface flow system will naturally attenuate faster than others. Similarly, it can be expected that the hydrologic processes affecting contaminant flushing and subsequent transport toward springs and creeks north of the plant area will be highly variable over time. As a consequence, contaminants dissolved in groundwater and spring water could be subject to alternating periods of concentration increases and decreases before persistent decreases in concentration are clearly observed. These topics are discussed further in the following section, which deals with the characterization of site hydrogeology and the associated monitoring of contaminant levels that have occurred during the past two decades.

2.2 Site Characterization and Monitoring

As early as the 1970s, work began on the description of hydrogeologic conditions in the chemical plant area and the identification of contaminants in the subsurface potentially resulting from historical plant operations. This characterization continued through the 1980s. Some of the early characterization efforts were accomplished by the U.S. Geological Survey (USGS) through a series of studies that looked not only at aquifer properties and subsurface flow processes but also at contaminant types that were present in the plant area due to features like the four raffinate pits that were used to store waste. For example, a report by Kleeschulte and Emmett (1987) summarized the results of several different investigations concerning the character of the shallow bedrock aquifer and identified preferential flow mechanisms for conveying groundwater to Burgermeister Spring and the tributaries to Dardenne Creek. This study also documented some tracer studies conducted by the Missouri Department of Natural Resources (MDNR) in the mid-1980s, which detected a relatively strong hydraulic connection between Burgermeister Spring and a tributary to Schote Creek, which is a losing stream. The Kleeschulte and Emmett investigation also identified several inorganic constituents, in both soil and groundwater, that were related to the leakage of water from one or more of the raffinate pits. Of the identified contaminants, the most notable were nitrate and uranium.

A USGS study by Schumacher (1993) provided a detailed assessment of the geochemistry of water in both groundwater and the overburden in the chemical plant area. Like the investigation by Kleeschulte and Emmett, this geochemical assessment focused on inorganic constituents, many of which could be primarily attributed to features in the plant area (most notably, the raffinate pits). In addition to examining inorganic components of wastewater and sludge in some of the raffinate pits, Schumacher described the degree to which a variety of geochemical factors could be expected to affect contaminant migration in the shallow bedrock aquifer. Observations made by Schumacher that had bearing on natural attenuation processes in the shallow bedrock aquifer included the following: (1) mostly, chemically oxidizing conditions are present in the shallow weathered portion of the shallow aquifer, and somewhat more reducing conditions are present in the unweathered zone; (2) the transport of nitrate is unlikely to be retarded due to sorption or its mass being reduced by biodegradation processes; (3) uranium is mobile in shallow groundwater (rather than occurring as a precipitated mineral) under the relatively oxidizing conditions present in the weathered zone; and (4) the transport of dissolved uranium species is

mildly to heavily retarded due to their sorption on aquifer and overburden sediments, and the degree of sorption varies depending on sediment type and general groundwater chemistry.

In the early 1990s, USGS began collecting data that were indicative of contamination by nitroaromatic compounds in both the overburden and the shallow bedrock aquifer. Schumacher et al. (1993) reported on detections of TNT, 2,4-DNT, 2,6-DNT, 1,3,5-trinitrobenze (1,3,5-TNB), and other nitroaromatics in water samples collected from lysimeters installed in the unsaturated overburden at the WSTA. The Schumacher et al. investigation also showed the presence of nitroaromatic compounds in groundwater sampled from wells at the WSTA as well as in a sample from Burgermeister Spring. A subsequent study by Schumacher et al. (1996) expanded on the previous study of nitroaromatics in the subsurface at the WSTA. Again, samples of soil moisture collected from lysimeters installed in the unsaturated overburden indicated the presence of a variety of nitroaromatic compounds. In addition, relatively high concentrations of nitroaromatic compounds were measured in samples from wells located immediately west of the chemical plant area, indicating that sources of the compounds may have been located on WSTA property just west of the chemical plant. The Schumacher et al. (1996) study also demonstrated that nitroaromatic compounds were present in springs located both north and south of the chemical plant area.

Mugel (1997), while summarizing much of the hydrogeologic characterization work that had been performed in previous years by the USGS and others, provided additional information that helped explain observations made regarding groundwater that discharged to surface water north of the chemical plant area. In particular, it was reported that the weathered zone of the shallow bedrock aquifer was largely absent, or very thin, north of the chemical plant area, which caused the uppermost part of the saturated zone in some locales to occur in overburden materials. In addition, the presence of a paleodrainage aligned with the unnamed tributary containing Burgermeister Spring helped explain why the channel of the unnamed tributary was capable of intersecting saturated portions of the overburden, thus allowing the tributary and springs like Burgermeister to act as sites of concentrated discharge for most, if not all, groundwater migrating north from the plant area.

The remedial investigation (RI) for the chemical plant GWOU was part of a combined RI for both the DA Ordnance Works and the chemical plant area (DOE and DA 1997). This report summarized much of the site characterization that USGS and contractors to the Army and DOE had conducted in previous years, as well as results from sampling events that the Army and DOE conducted in 1995 as part of the joint RI effort. The joint Army and DOE groundwater RI contained detailed descriptions of the nature and extent of subsurface contamination that was determined to be the result of historical operations at the former WSOW and the chemical plant area. The RI described site areas of concern for groundwater contamination of dissolved nitrate, uranium, trichloroethylene (TCE), and nitroaromatic compounds. The combined RI summarized various processes and geochemical factors that were expected to play roles in the eventual fate of the COCs in site groundwater and overburden. Uranium, nitrate, and nitroaromatic compounds were also reported for Burgermeister Spring and Southeast Drainage springs.

The combined RI also summarized the hydrogeologic conceptual model of the WSTA and chemical plant area as developed through multiple years of field investigations. Hydraulic conductivities in the weathered portion of the Burlington-Keokuk Limestone were described as being highly variable, ranging from as low as 1×10^{-7} centimeters per second (cm/s) to as high

as 1×10^{-2} cm/s. Hydraulic conductivities in the underlying unweathered zone were described as being much lower in value than those observed in the weathered zone, varying from 10^{-7} to 10^{-5} cm/s. Though the hydraulic conductivity of overburden materials was generally characterized as being much lower than the hydraulic conductivity of the weathered zone of the bedrock aquifer, hydraulic conductivity values approaching and even exceeding those observed for the weathered bedrock zone were attributed to materials comprising the residuum at the bedrock/overburden contact. Portions of the RI describing the local hydrogeology also focused on the results of tracer investigations that had been performed by MDNR in earlier years (e.g., MDNR 1991) and studies performed during the RI that documented a strong hydraulic connection between groundwater in parts of the chemical plant area and Burgermeister Spring. A very small travel time of 48 to 72 hours was associated with some preferential flow paths connecting the north portion of the plant area and Burgermeister Spring, located more than a mile to the north of the chemical plant's north boundary.

During the many years that hydrogeologic and contaminant characterization has been carried out in and near the plant area, numerous monitoring wells have been installed with the intent of better describing the nature and extent of subsurface contamination. Most groundwater wells have been completed in the Burlington-Keokuk Limestone, particularly in the weathered zone where the potential for groundwater contamination is the greatest. Some wells screened in the unweathered zone of the Burlington-Keokuk Limestone have been installed to assess the potential for the vertically downward migration of contaminants. Where possible, monitoring wells within the boundaries of the chemical plant area have been mostly located near former contaminant sources and preferential flow pathways (paleochannels), and several additional wells have been placed outside the chemical plant boundary to detect the possible off-site migration of contaminants.

At one time, more than 100 wells were available in the vicinity of the chemical plant area for monitoring groundwater flow and contaminant behavior. By the early 2000s, the total number of monitoring wells in and near the plant area had been reduced to 86 (DOE 2003). A map view of the locations of monitoring wells that were being used in 2002 is presented in Figure 2−8. The distribution of the wells is indicative of logic that has been repeatedly applied over the years not only to track the COCs in groundwater but also to assess the different types of transport behavior that can occur along preferential pathways and areas of relatively low permeability.

The demonstrated hydraulic connection between groundwater in the chemical plant area and neighboring springs led to the monitoring of several of those springs in the years following the RI. This monitoring has generally been limited to three locations adjacent to an unnamed tributary to Dardenne Creek (SP-6301, SP-6303, and SP-6306) and two springs in the Southeast Drainage (SP-5303 and SP-5304). The locations of these springs are shown in Figure 2–9. Location SP-6301 corresponds to Burgermeister Spring. Spring SP-6306, which is monitored occasionally in response to public comments, remains unaffected by site contaminants.

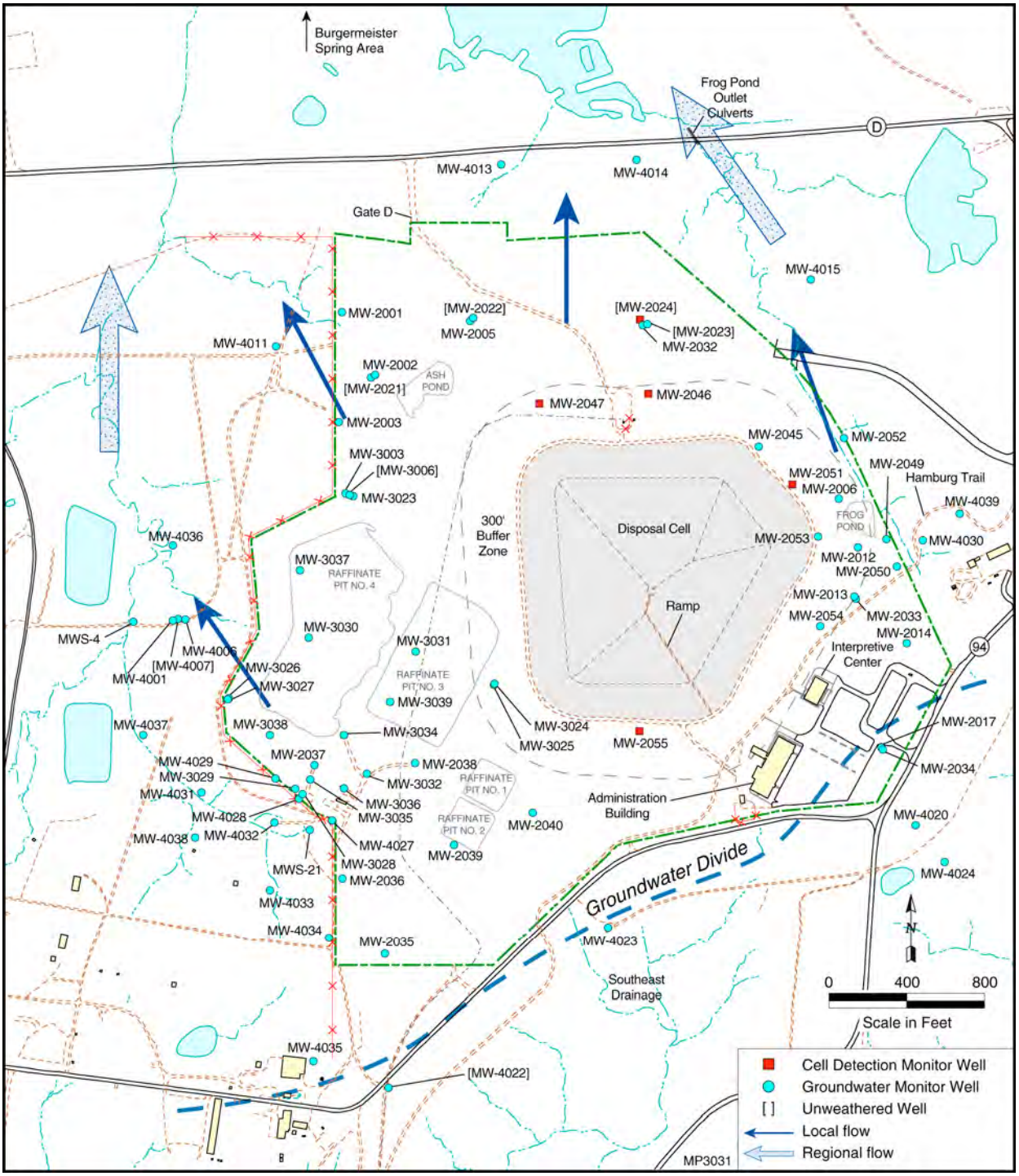

Figure 2–8. Monitoring Wells in the Chemical Plant Area in 2002

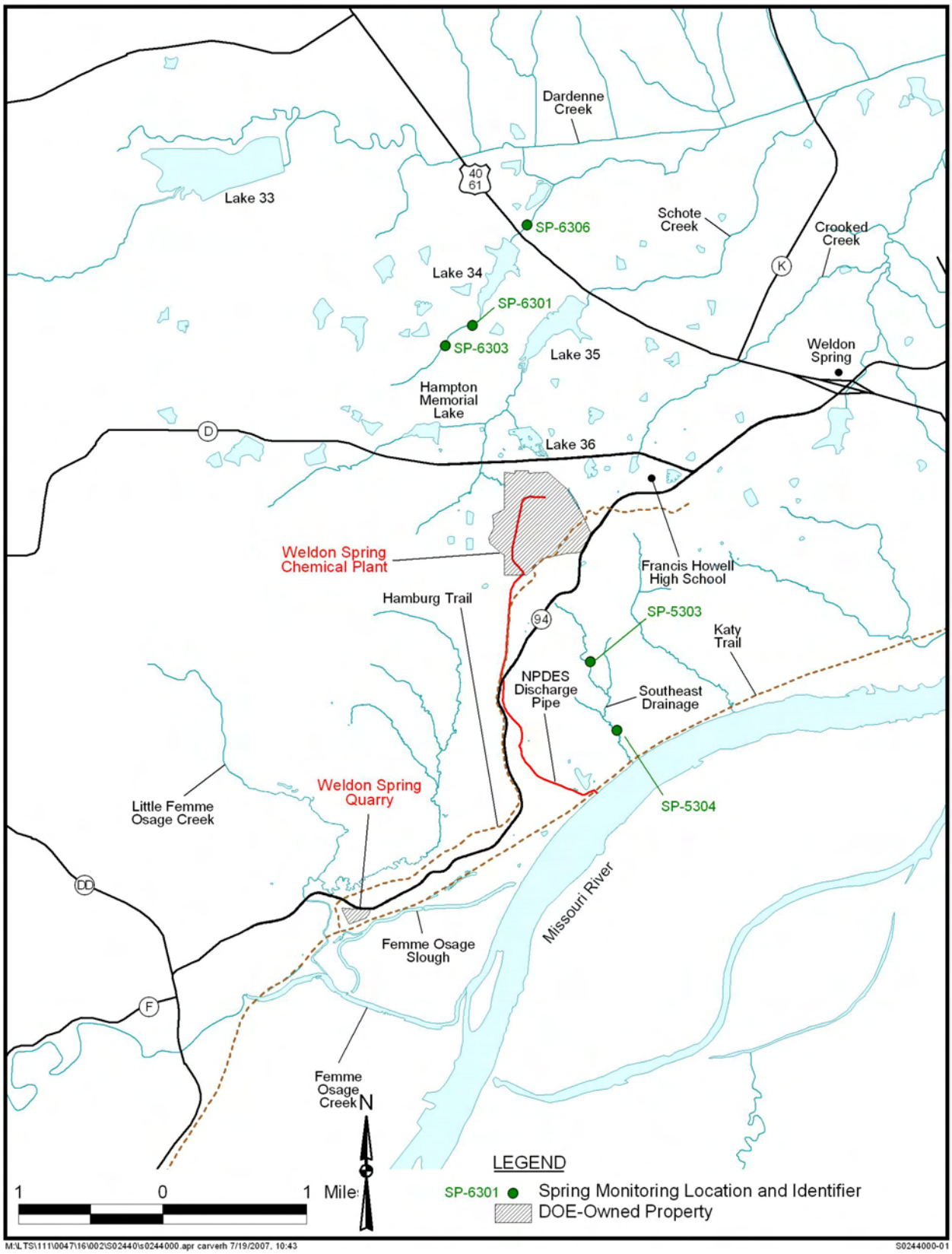

Figure 2–9. Spring Monitoring Locations in the Vicinity of the Chemical Plant in 2002

2.3 Studies Conducted Prior to the Implementation of MNA

Several field studies were conducted before the selection and implementation of the MNA remedy. Two of the studies determined that potential approaches to accelerating aquifer remediation were likely to be limited by the complex hydrogeology of the chemical plant area. To support the selection of MNA, estimates of timeframes to meet remedial action objectives (RAOs) for the COCs were also performed for the RI/feasibility-study phase; the table of timeframes and the table summarizing the RAOs are reproduced in this report.

2.3.1 Additional Groundwater Field Studies—Enhanced Groundwater Extraction

Field studies of enhanced means of extracting groundwater from the shallow bedrock aquifer (DOE 2002) were a continuation of a pumping investigation performed years earlier (DOE 1998a) that suggested that very low sustainable withdrawal rates from the aquifer would be typical. Consequently, variations on conventional groundwater extraction from wells were evaluated in the field investigations. The variations included (1) the use of angled wells that have a higher probability of intersecting vertical fractures and (2) the use of water injection in combination with well pumping.

Several monitoring locations were used to conduct and evaluate tests of enhanced groundwater extraction (Figure 2–10). Included in the suite of locations were four monitoring wells (MW-3034, MW-3035, MW-3036, MW-4032) that were specifically drilled and constructed to support the tests. In addition, two angled boreholes were drilled for the tests. One of the angled boreholes (AH-2007) was converted into a monitoring well (MW-3033) and was abandoned after the tests. The other angled borehole (AH-2006) was not utilized for the study and was subsequently abandoned. All of the testing was performed in an area located about 500 ft south of former raffinate pits 3 and 4, close to the chemical plant area boundary. This area was also situated within one of the preferential flow zones shown in Figure 2–6.

The results of the field studies indicated that modifications to conventional systems for extracting groundwater would not increase the rate of COC removal from that achieved by pumping from vertical wells alone (DOE 2002). More specifically, it was concluded that the amount of water extracted from the test area as a result of artificial recharge would not reduce the remediation time frames for TCE, nitrate, uranium, or nitroaromatic compounds in the area. Likewise, the use of an angled well failed to produce results comparable to those achieved by a vertical extraction well. These observations, which were consistent with findings from the previous study of groundwater extraction (DOE 1998b), were representative of universal difficulties involved in siting productive wells in the chemical plant area. As a result of the field investigation, the hydrogeologic conceptual model of the site remained the same, wherein sustainable aquifer yields are assumed to be low (generally less than 3 gallons per minute [gpm] per well) and recharge to the aquifer is slow.

The field investigations demonstrated the difficulty of using artificial recharge effectively in a heterogeneous, fractured medium. Poor hydraulic connections between locations were indicated by (1) significant groundwater mounding at injection sites, (2) dissimilar hydraulic responses at two injection wells in close proximity (< 300 ft) to each other, (3) the incomplete capture of injection water despite the fact that injection wells were within the hydraulic capture zone of extraction wells, and (4) limited increases in pumping rates from extraction wells during periods of water injection.

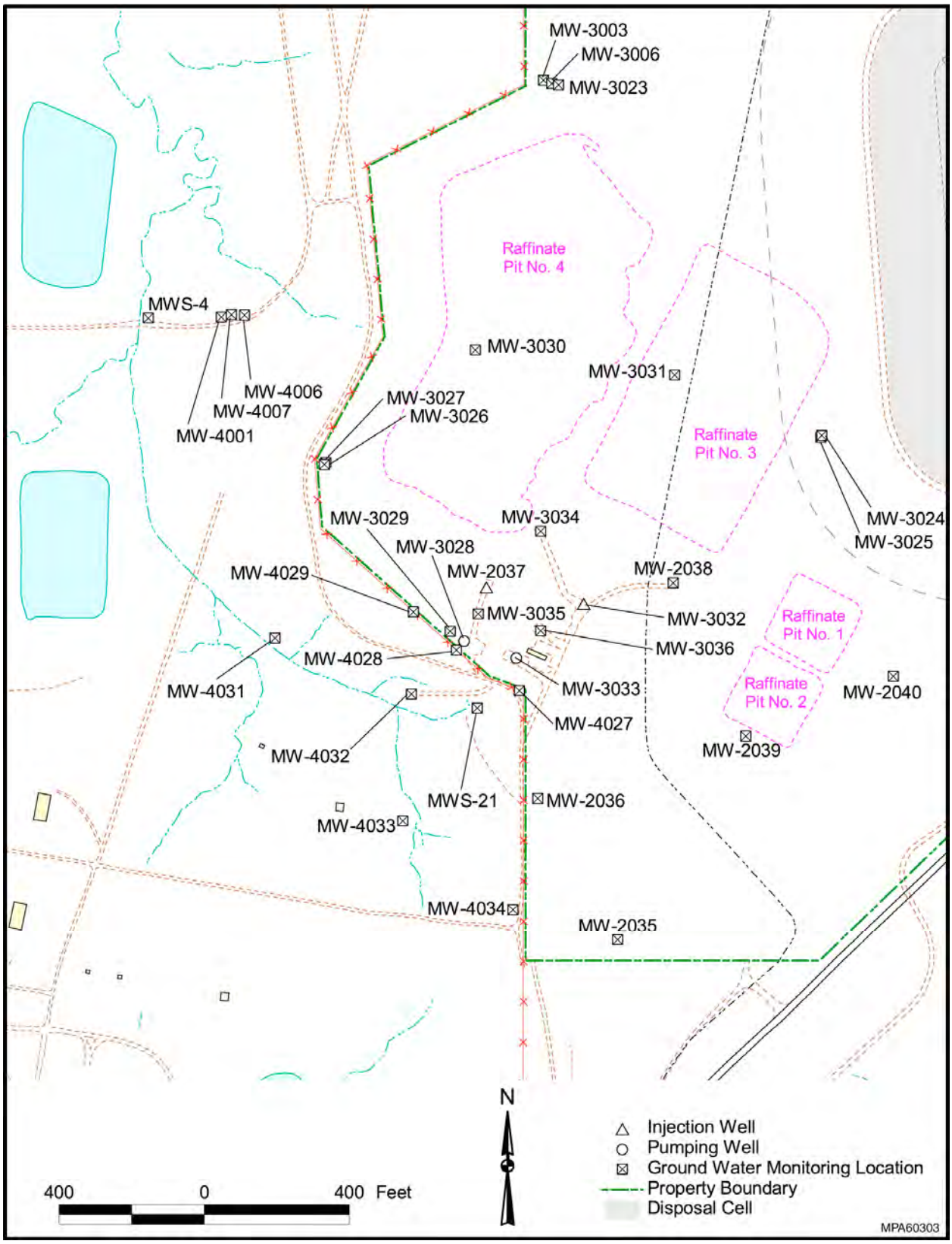

Figure 2–10. Locations of Wells Used for the Enhanced Groundwater Extractions Tests

Other evidence for the "compartmentalization" of groundwater in the shallow bedrock aquifer was observed largely as a result of pumping alone. Attempts to construct maps of the potentiometric surface caused by pumping indicated that the induced drawdown did not extend radially from a well and tended to be greater in the direction of the orientation of the preferential flow pathway tapped by the well. In addition, recovery of the groundwater levels in the shallow aquifer upon completion of pumping was very slow. Five months after the cessation of pumping, water levels in the study area ranged from 0.3 to 1.0 ft (9 to 30 cm) below water elevations recorded prior to the testing.

Some mobilization of contaminants was observed as a result of the water injection. Increasing concentrations of nitrate were observed in some monitoring wells located hydraulically downgradient of injection sites, as were nitrate concentrations in springs SP-6301 (Burgermeister Spring) and SP-6303. However, the contaminant concentrations observed in the springs did not approach historical highs.

With the exception of the short-term dilution of dissolved contamination in the vicinity of injection sites, the effects of injection on contaminant concentrations were observed to be minor. Contaminant concentrations in monitoring wells returned to pre-testing levels or were showing increasing trends when test monitoring came to an end. Such observations highlighted the generally slow, but persistent, transport of contaminated groundwater from less permeable zones into preferential flow pathways after the flushing of those pathways.

2.3.2 In Situ Chemical Oxidation (ICO) of TCE

Pilot testing of an ICO process for reducing concentrations of TCE in chemical plant groundwater (DOE 2004a) was conducted during the spring and early summer of 2002. This project involved the injection of an oxidant in the form of a chemical solution (permanganate solution) into groundwater, with the intent of chemically transforming dissolved TCE into benign products. Bench tests performed by several vendors prior to the pilot testing indicated that this process was relatively effective in treating TCE on a laboratory scale. However, it was less clear whether the implementation of ICO would be effective when applied to the complex flow system associated with the shallow bedrock aquifer in the plant area.

The pilot tests were performed in an area located south of former raffinate pits 3 and 4, in the same general area tested for enhanced groundwater extraction (DOE 2002). As with the enhanced groundwater extraction tests, numerous wells were used to conduct and evaluate the ICO tests (Figure 2–11). Two injection wells (HIW1 and LIW1) and six monitoring wells (ICO-1 through ICO-6) were installed in support of the pilot-phase ICO testing. All of the wells were installed through the full thickness of the weathered portion of the Burlington-Keokuk Limestone. Packer tests conducted prior to the pilot investigation indicated that one of the injection wells was located in an area of relatively high permeability and the other was screened in an area of considerably lower permeability. The testing in two differing hydraulic conductivities was a design criterion for the pilot study. In general, ICO was found to have a limited effect on TCE concentrations in the tested area, and the limited success of the project was largely attributed to the complex hydrogeology of the site. The injected permanganate solution in both the high and low permeability locales appeared to migrate in irregular patterns from the injection sites, following preferential flow directions.

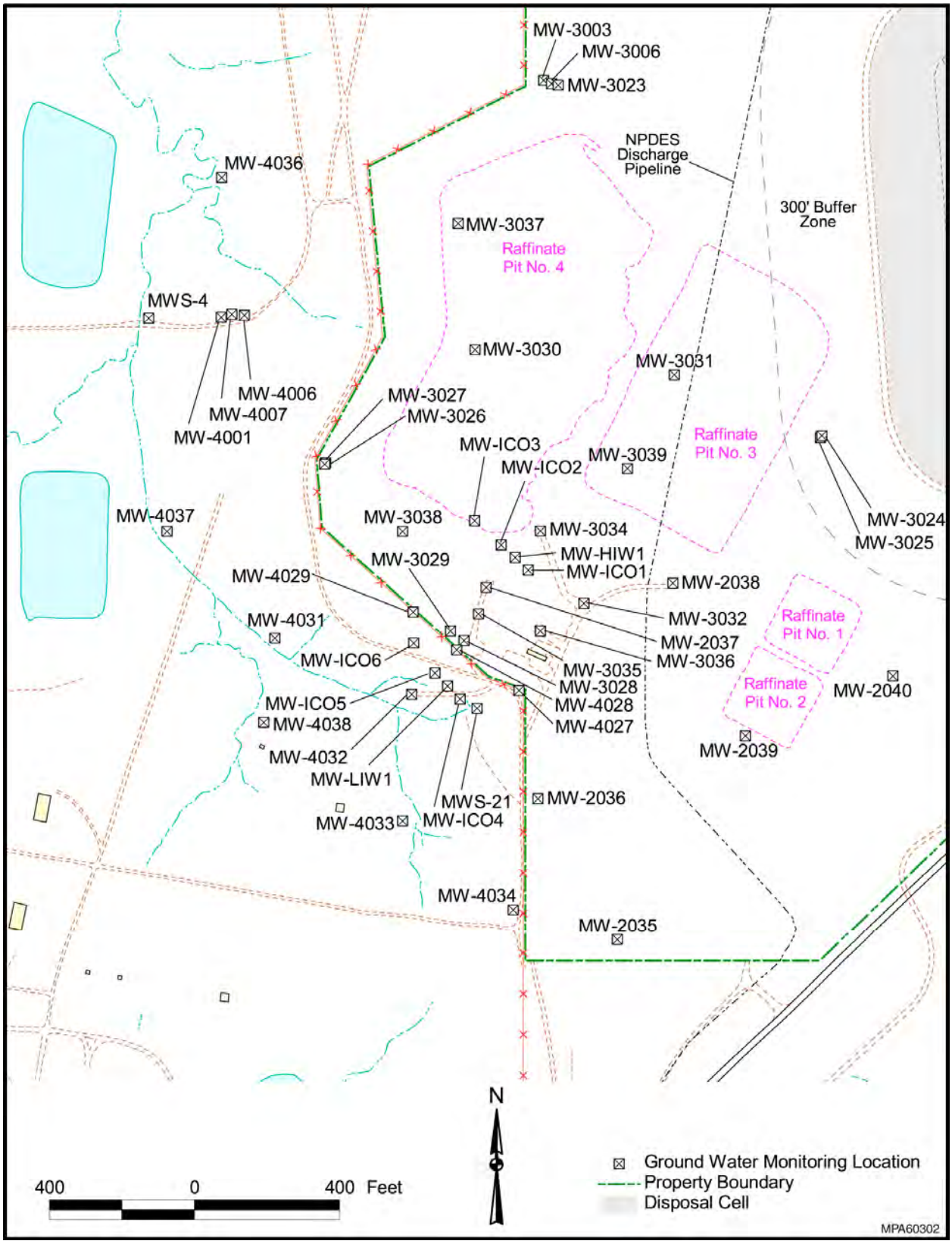

Figure 2–11. Locations of Wells Used for Pilot Tests of In Situ Chemical Oxidation

In addition, the area influenced by permanganate injection in the area of lower permeability was considerably smaller than the affected zone in the high permeability area, indicating that chemical methods for enhancing aquifer remediation would be of limited utility for the chemical plant area as a whole. Though ICO temporarily reduced TCE concentrations in the respective areas of influence, data collected from monitoring wells after injections showed TCE reappearing at the same levels measured prior to the testing. The pilot-phase ICO also indicated that the volume of permanganate solution required to affect oxidized zones necessary for remediating the full area impacted by TCE contamination would be much larger than bench-scale testing had previously suggested. Such results were characteristic of a subsurface flow and transport system influenced by strong heterogeneity over short distances, in which short-term reductions in COC concentration are subsequently reversed due to the gradual influx of contaminated water from unaffected low-permeability zones.

2.3.3 MNA Timeframe Calculations

Modeling to estimate timeframes for MNA to meet remedial objectives was performed using data representative of site conditions in 2002 (DOE 2003). The resulting calculations suggested that MNA would be achieved in about 100 years. These estimates, along with the results of the enhanced groundwater extraction study and ICO of TCE, were taken into consideration. MNA was concluded to be an effective approach for attaining the RAOs. The table of MNA timeframe estimates is reproduced as Table 2–1 in this report.

2.4 MNA Monitoring Program

The RD/RA work plan (DOE 2004b) presented the foundation of the natural attenuation monitoring network that would be implemented for the GWOU. The designated network, consisting of both wells and springs, was designed to meet six separate objectives:

- Objective 1 is to monitor the unaffected water quality at upgradient locations in order to maintain a baseline of naturally occurring constituents from which to evaluate changes in downgradient locations. This objective will be met by using wells located upgradient of the contaminant plume.
- Objective 2 is to verify that contaminant concentrations are declining at a rate and in a manner that cleanup standards (Table 2–2) will be met in approximately 100 years, as established by predictive modeling. This objective will be met using wells at or near the locations with the highest concentrations of contaminants, both near the former source areas and along expected migration pathways. The objective will be to evaluate the most contaminated zones. Long-term trend analysis will be performed to confirm downward trends in contaminant concentrations over time. Performance will be gauged against long-term trends. Some locations are expected to show temporary upward trends due to the recent source control remediation, ongoing dispersion, seasonal fluctuations, analytical variability, or other factors. However, concentrations are not expected to exceed historical maximums.

Table 2–1. Computed Times to Cleanup with the MNA Remedy [a]

Contaminant	Contour/Area	Wells Included	Distribution Coefficient K_d (mL/g)	Retardation Factor[b] R (-)	Hydraulic Conductivity K (cm/s)	Plume Length L(ft)	Hydraulic Gradient (-)	Initial Conc. C_o	RAO C_w	Cleanup Time (years)
Nitrate	Contour 1 Area 1	4036, 3037, 4006, 4001, 3030, 3031, 3027, 3026, 3039, 3025, 4027, 3038, 3034, 2037, 2038, 4029, 3035, 3032, 3028, 3029, 3036, 4031, 4028, 3033, 4038, 4032	0	1.0	0.00315	2750	0.006	198 mg/L	10 mg/L	63
	Area 2	4013, 2001, 2005, 4011, 2021, 2002, 2047, 2003, 3003, 3023	0	1.0	0.00173	2350	0.02	173 mg/L	10 mg/L	28
Uranium	Contour 1	3030	0.4	5.5	0.0012	1050	0.0125	54 pCi/L	20 pCi/L	56
	Contour 2	3025	0.4	5.5	0.003	460	0.0125	29 pCi/L	20 pCi/L	4
TCE	Contour 1	4006, 4001, 3030, 3025, 4037, 3039, 3034, 2037, 2038, 4029, 3035, 4031, 3036, 3029, 3028, 4028, 3033, 4027, 4032, MWS-21, 4038, 3032	0.3	4.4	0.00411	1300	0.005	61 µg/L	5 µg/L	101
2,4-DNT	Contour 1	3038, 2037, 4029, 3035, 3029, 3028, 4028, 3033, 4032, MWS-21, 4033, 4006, 4001, 3030, 3039, 3034, 2038	0.09	2.0	0.001	1600	0.008	0.43 µg/L	0.11 µg/L	79
	Contour 2	2047, 2046	0.09	2.0	0.00104	400	0.006	0.18 µg/L	0.11 µg/L	9
	Contour 3	2052, 2006, 2053, 2054, 2013, 2012, 2049, 2050, 2033, 4030, 2014	0.09	2.0	0.00352	1400	0.011	114 µg/L	0.11 µg/L	73
2,6-DNT	Contour 1	4036, 4006, MWS-4, 4001, 3030, 3039, 3034, 4037, 3038, 4031, 4029, 3029, 3028, 4028, 3033, 3036, 4027, 4032	0.2	3.3	0.0012	1700	0.0119	0.34 µg/L	1.3 µg/L	NA
	Contour 2	2002, 2003, 3003, 3023	0.2	3.3	0.00019	1050	0.0167	0.41 µg/L	1.3 µg/L	NA
	Contour 3	2005	0.2	3.3	0.000021	400	0.0125	0.27 µg/L	1.3 µg/L	NA
	Contour 4	2047, 2046	0.2	3.3	0.00104	500	0.0125	0.81 µg/L	1.3 µg/L	NA
	Contour 5	4015, 2045, 2052, 2051, 2006, 2053, 2049, 2012, 4030, 4039, 2050, 2013, 2033, 2054, 2014	0.2	3.3	0.00341	2300	0.0236	66 µg/L	1.3 µg/L	53
2,4,6-TNT	Contour 1	2046	0.04	1.5	0.0014	400	0.05	4.2 µg/L	2.8 µg/L	1
	Contour 2	2053, 2049, 2012	0.04	1.5	0.00396	350	0.0125	75 µg/L	2.8 µg/L	5
1,3-DNB	Contour 1	2012	0	1.0	0.001	500	0.011	1.7 µg/L	1 µg/L	4
NB	Contour 1	2012	0	1.0	0.001	500	0.011	69 µg/L	17 µg/L	9

[a]The table presented in ANL (2003a) included estimates for 2,6-DNT with an RAO of 0.13 µg/L. The RAO for 2,6-DNT was subsequently established in the Record of Decision (ROD) (DOE 2004c) as 1.3 µg/L, and the calculations in this table reflect this change.
[b]Retardation factor calculated using a dry bulk density of 1.7 g/mL and an effective porosity of 0.15.
NA = not applicable
mL/g = milliliters per gram

Table 2–2. Cleanup Standards for the GWOU

COC	Cleanup Standard	Basis of Cleanup Standard
TCE	5 µg/L	Chemical-specific ARAR based on federal MCL for drinking water.
Nitrate (as N)	10 mg/L	Chemical-specific ARAR based on federal MCL for drinking water.
Uranium	20 pCi/L[a]	Chemical-specific ARAR based on federal MCL for drinking water.
2,4-DNT	0.11 µg/L	Chemical-specific ARAR based on State of Missouri water quality standards.
1,3-DNB	1.0 µg/L	Chemical-specific ARAR based on State of Missouri water quality standards.
NB	17 µg/L	Chemical-specific ARAR based on State of Missouri water quality standards.
2,6-DNT	1.3 µg/L [b]	Risk-based concentration equivalent to 10^{-5} for a resident scenario.
2,4,6-TNT	2.8 µg/L	Risk-based concentration equivalent to 10^{-6} for a resident scenario.

[a]20 pCi/L is equivalent to 30 µg/L based on isotopic ratios of uranium established for the Weldon Spring Site.
[b]On the basis of site-specific factors, including technical limitations in achieving cleanup levels more stringent than a 10^{-5} risk level, the remedial goal for 2,6-DNT is set at 1.3 µg/L, which corresponds to the 10^{-5} risk level.

Key: µg/L = micrograms per liter, pCi/L = picocuries per liter, MCL = maximum contaminant level, mg/L = milligrams per liter, ARAR = applicable or relevant and appropriate requirement

- Objective 3 is to ensure that lateral migration remains confined to the current area of impact. Contaminants are expected to continue to disperse within known preferential flow paths associated with bedrock lows (paleochannels) in the upper Burlington-Keokuck Limestone and become more dilute over time as rain events continue to recharge the area. This objective will be met by monitoring various downgradient fringe locations that either are not impacted or are minimally impacted. Contaminant impacts in these locations are expected to remain minimal or nonexistent.
- Objective 4 is to monitor locations underlying the impacted groundwater system to confirm that there is no significant vertical migration of contaminants. This will be evaluated using deeper wells screened and influenced by the unweathered zone. No significant impacts at these locations should be observed.
- Objective 5 is to monitor contaminant levels at the impacted springs that are the only potential points of exposure under current land use conditions. The springs discharge groundwater that includes contaminated groundwater originating at the chemical plant area. Presently, contaminant concentrations at these locations are protective of human health and the environment under current recreational land uses. The continued improvement of the water quality in the affected springs should be observed.
- Objective 6 is to monitor for hydrologic conditions at the site over time in order to identify any changes in groundwater flow that might affect the protectiveness of the selected remedy. The static groundwater elevation of the monitoring network will be measured to establish that groundwater flow is not changing significantly and resulting in changes in contaminant migration.

The final Record of Decision (ROD) (DOE 2004c) established MNA as the GWOU remedy and presented the preceding objectives for guiding the performance evaluation of natural attenuation. The RD/RA work plan identified specific wells and springs in and near the chemical plant area that were to be used for evaluating the natural attenuation of each of the COCs. A total of 41 wells were designated for MNA monitoring—significantly fewer than the 86 wells used in 2002 (Figure 2−8) to delineate COC plumes and estimate times to cleanup as a result of natural dilution and dispersion processes (DOE 2003). Monitoring in accordance with the RD/RA work plan began in July 2004.

An interim remedial action (IRA) report was prepared (DOE 2005a) in accordance with the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) to summarize the construction activities and evaluate the adequacy of the monitoring network for the GWOU. This included reporting on the findings from the installation of four new monitoring wells that had been outlined in the RD/RA work plan. Two of the wells, MW-3040 and MW-4040, were installed in the unweathered zone of the Burlington-Keokuk Limestone in the vicinity of former raffinate pits 3 and 4. A third well, MW-2056, was installed in the unweathered zone about 800 ft north of Frog Pond; the fourth, MW-4041, was located approximately 4,000 ft north of the chemical plant's north boundary, apparently within a preferential flow zone leading to Burgermeister Spring. The first three of these wells were intended as Objective 4 wells under the assumption that COCs would not be detected in the unweathered zone below the former raffinate pits and the area surrounding Frog Pond. Although this proved to be the case at MW-2056 north of Frog Pond, uranium and nitrate at levels above the MCL were detected in MW-3040 and MW-4040 in the raffinate pits area.

It was concluded in the IRA report that modifications to the network were necessary to meet the monitoring objectives. As a result, it was recommended in the IRA report that MW-30340 and MW-4040 be used as Objective 2 wells instead of Objective 4 wells. In addition, MW-2056 remained an Objective 4 monitoring location, and MW-4041 became an Objective 3 location. One additional well in the unweathered zone, MWD-2, was added as an Objective 4 well because neither MW-3040 nor MW-4040 could be used for this objective. These steps resulted in a final monitoring network for MNA that consisted of the wells, the springs, and one surface-water location listed in Table 2–3. A map showing the locations of all components of this monitoring network is presented in Figure 2–12.

Table 2–3. Monitoring Locations Retained for Assessing MNA at the GWOU

Objective 1	Objective 2	Objective 3	Objective 4	Objective 5	Objective 6
MW-2017	MW-2012	MW-2032	MW-2021	SP5303	MW-2005
MW-2035	MW-2014	MW-2051	MW-2022	SP5304	MW-2055
MW-4022	MW-2038	MW-3031	MW-2023	SP6301	MW-3025
MW-4023	MW-2040	MW-3037	MW-2056	SP6303	MW-3038
	MW-2046	MW-4013	MW-3006	SW-2007[b]	MW-4001
	MW-2050	MW-4014	MW-4007		MW-4011
	MW-2052	MW-4015	MWD-2		MW-4020
	MW-2053	MW-4026			MW-4037
	MW-2054	MW-4036			
	MW-3003	MW-4039			
	MW-3024	MW-4041			
	MW-3030	MWS-1			
	MW-3034	MWS-4			
	MW-3039				
	MW-3040				
	MW-4013[a]				
	MW-4029				
	MW-4031				
	MW-4036[a]				
	MW-4040				

[a]Location is also an Objective 3 location.
[b]Location is on Dardenne Creek immediately upstream of Highway 40/61, approximately 2.1 miles north of the site.

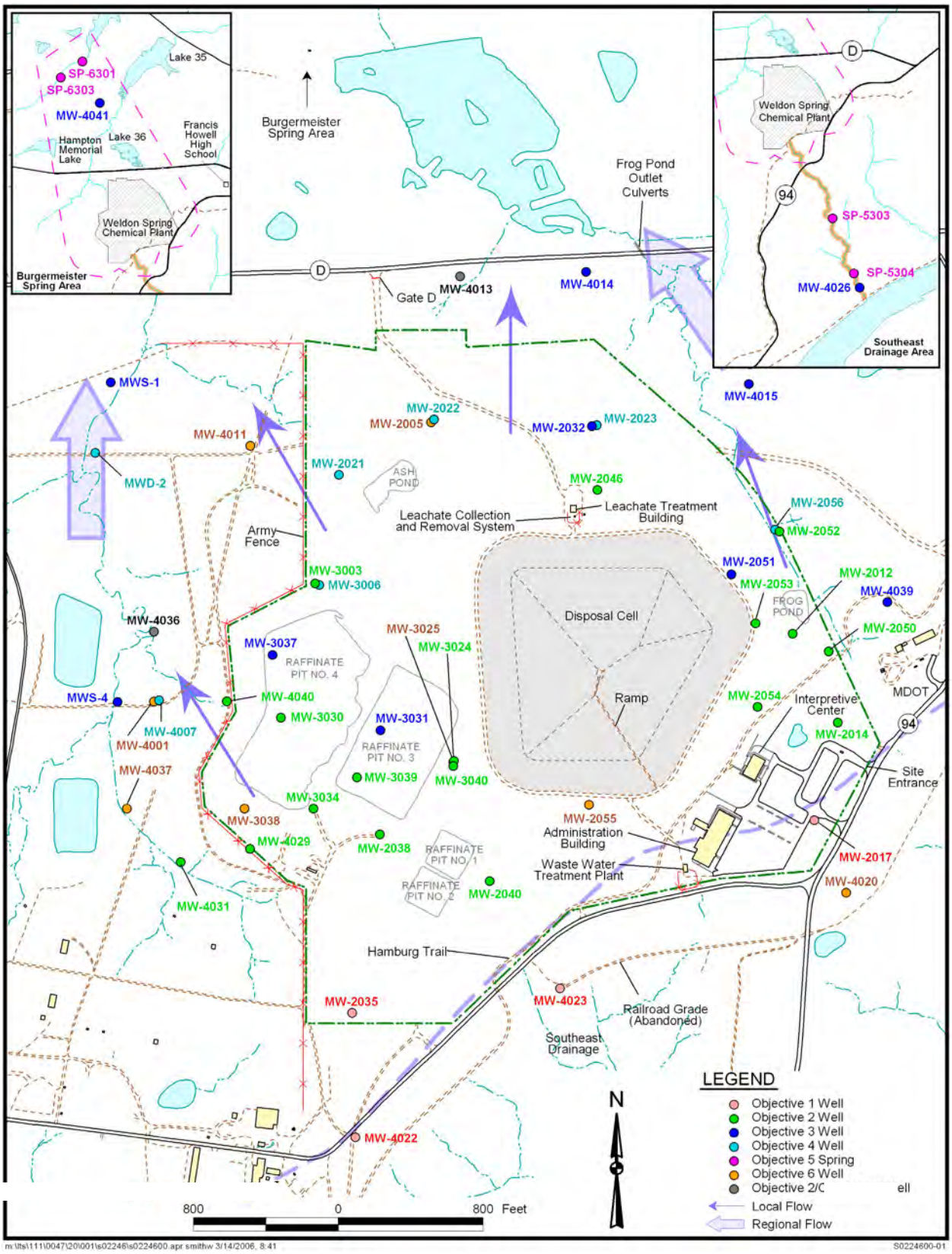

Figure 2–12. Monitoring Well Network for Evaluating MNA

The final monitoring network contains 52 wells, some of which are used to track multiple COCs. A few of the Objective 2 wells are also used for Objective 3 purposes (Table 2–3) depending on the COC. The MNA network also includes four of the five springs that were regularly monitored as of 2002 (Figure 2–9). In addition, one surface water sampling location on Dardenne Creek, about 2.1 miles north of the site, is included in the monitoring system.

During baseline sampling, the sampling frequency at MNA wells varies with the monitoring location. Most of the wells are sampled semiannually, as are the four springs. Exceptions to this rule include the four wells that were installed to fill data gaps (MW-2056, MW-3040, MW-4040, MW-4041), which are currently sampled quarterly. Additional locations that are sampled quarterly include wells MW-2022, MW-2023, MWS-1, MWS-4, and MWD-2 and the surface water monitoring site on Dardenne Creek. Quarterly sampling was performed during the baselining period in order to provide a data set of sufficient size (minimum of 8 data points) to perform statistics. Table 2–4 lists these monitoring frequencies along with the COCs that are sampled at each monitoring location.

Table 2–4. Monitoring Parameters for MNA Locations

Location	Sampling Frequency[a]	Monitoring Parameters							
		TCE	Nitrate (as N)	Uranium	1,3-DNB	2,4,6-TNT	2,4-DNT	2,6-DNT	NB
MW-2012	S				✔	✔	✔	✔	✔
MW-2014	S						✔	✔	
MW-2017	S				✔	✔	✔	✔	✔
MW-2021	S		✔						
MW-2022	Q		✔		✔	✔			
MW-2023	Q				✔	✔	✔	✔	✔
MW-2032	S				✔	✔	✔	✔	✔
MW-2035	S	✔	✔	✔			✔		
MW-2038	S		✔				✔		
MW-2040	S		✔			✔			
MW-2046	S					✔			
MW-2050	S						✔	✔	
MW-2051	S				✔	✔	✔	✔	✔
MW-2052	S						✔	✔	
MW-2053	S					✔	✔	✔	
MW-2054	S						✔	✔	
MW-2056	Q				✔	✔	✔	✔	✔
MW-3003	S		✔	✔					
MW-3006	S	✔	✔	✔			✔		
MW-3024	S			✔					
MW-3030	S	✔		✔			✔		
MW-3031	S	✔		✔					
MW-3034	S	✔	✔				✔		
MW-3037	S	✔		✔			✔		
MW-3039	S						✔		
MW-3040	Q	✔	✔	✔					
MW-4007	S	✔	✔						
MW-4013	S		✔				✔	✔	✔
MW-4014	S		✔		✔	✔	✔	✔	✔
MW-4015	S						✔	✔	✔
MW-4022	S		✔	✔					
MW-4023	S		✔	✔					
MW-4026	S			✔					
MW-4029	S	✔	✔						
MW-4031	S		✔						
MW-4036	S	✔	✔	✔			✔		
MW-4039	S				✔	✔	✔	✔	✔
MW-4040	Q	✔	✔	✔			✔		
MW-4041	Q	✔	✔	✔	✔	✔	✔	✔	✔
MWS-1	Q	✔	✔	✔			✔		
MWS-4	Q	✔	✔	✔					
MWD-2	Q		✔	✔					
SP-5303	S			✔					
SP-5304	S			✔					
SP-6301	S	✔	✔	✔	✔	✔	✔	✔	✔
SP-6303	S	✔	✔	✔	✔	✔	✔	✔	✔
SW-2007	Q			✔					

[a]S = semiannually, Q = quarterly

3.0 Assessment of Baseline Data

3.1 Groundwater Levels

Monitoring of water levels during the last 5 years in the chemical plant area wells indicates that the flow directions inferred by the potentiometric surface of the shallow groundwater flow system have remained relatively constant. As suggested by the contoured water level surface in Figure 2−7, groundwater flow is generally toward the north within the chemical plant area's boundaries, and some groundwater flows to the northwest near the plant's west boundary. The bedrock topography provides some control over groundwater movement, particularly in the paleochannel areas. Though increases or decreases in groundwater elevation of up to about 0.5 ft are occasionally measured in individual monitoring wells between successive monitoring events, the general flow direction appears to remain constant. As a consequence, it seems unlikely that contaminant advection for the plant area as a whole and over the long term will be strongly affected by hydraulic stresses such as recharge events associated with storms. Similarly, natural attenuation processes in the shallow aquifer should not be drastically affected by changes in groundwater flow conditions.

3.2 Baseline Monitoring Data

This section presents the contaminant data from the baseline period and describes the spatial distribution of nitrate (as N), uranium, TCE, and nitroaromatic compounds (2,4-DNT, 2,4-DNT, and 2,4,6-TNT) in groundwater at the chemical plant. Baseline data was collected in order to establish a comprehensive set of data for the long-term monitoring locations. The distribution of the COCs shows the spatial extent relative to existing wells. The spatial extent of the COCs in groundwater is important because the ability of each contaminant to eventually flush from the shallow bedrock aquifer is influence by the proximity of the plume to preferential flow paths (paleochannels) that extend northward from the site (Figure 2–6).

3.2.1 Nitrate (as N)

The highest concentrations of nitrate have typically been measured in the vicinities of the raffinate pits and Ash Pond, which are the historical sources of this contaminant (Figure 3–1 and Figure 3–2). The higher mobility of nitrate, in comparison to other contaminants at the site, has resulted in a large distribution in the shallow aquifer. Nitrate levels exceed the MCL of 10 mg/L (for nitrate as N) in both the weathered and unweathered units of the Burlington-Keokuk Limestone.

Nitrate concentrations are highest in the weathered unit of the Burlington-Keokuk Limestone (Table 3–1). The highest concentrations in the weathered unit are measured in wells that are located in the former raffinate pit area (MW-2038, MW-3034, and MW-4029). Since baseline monitoring began, wells MW-2038 and MW-3034 have shown a decline. Well MW-4029 has increased slightly over the baselining period; however, this well is situated along a preferential flow pathway immediately downgradient of the raffinate pits. The other wells have lower nitrate impact. Well MW-4036, downgradient of former raffinate pit 4, exhibited a decrease below the MCL in 2006.

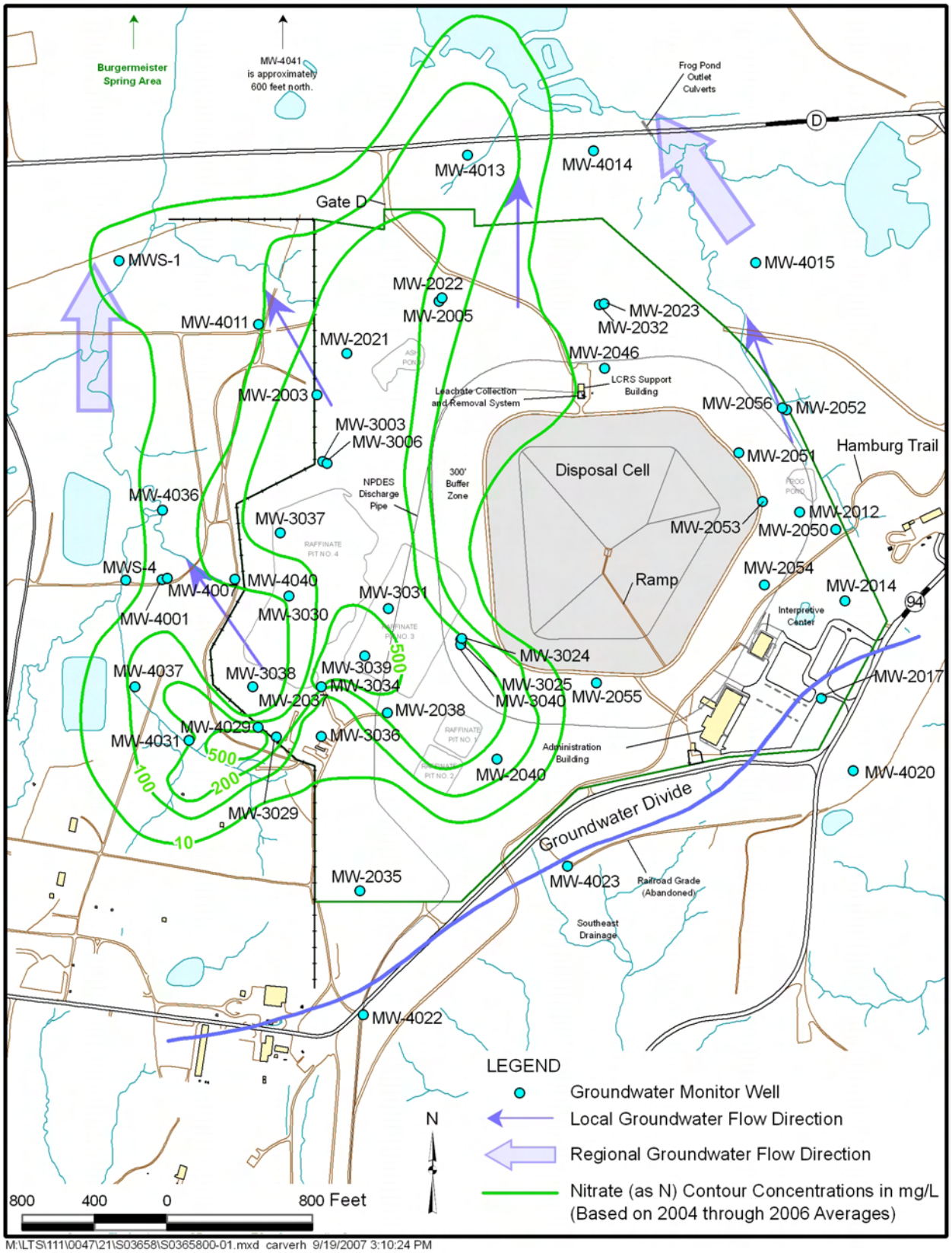

Figure 3–1. Distribution of Nitrate (as N)—Weathered Unit—MNA Baseline Data (2004−2006)

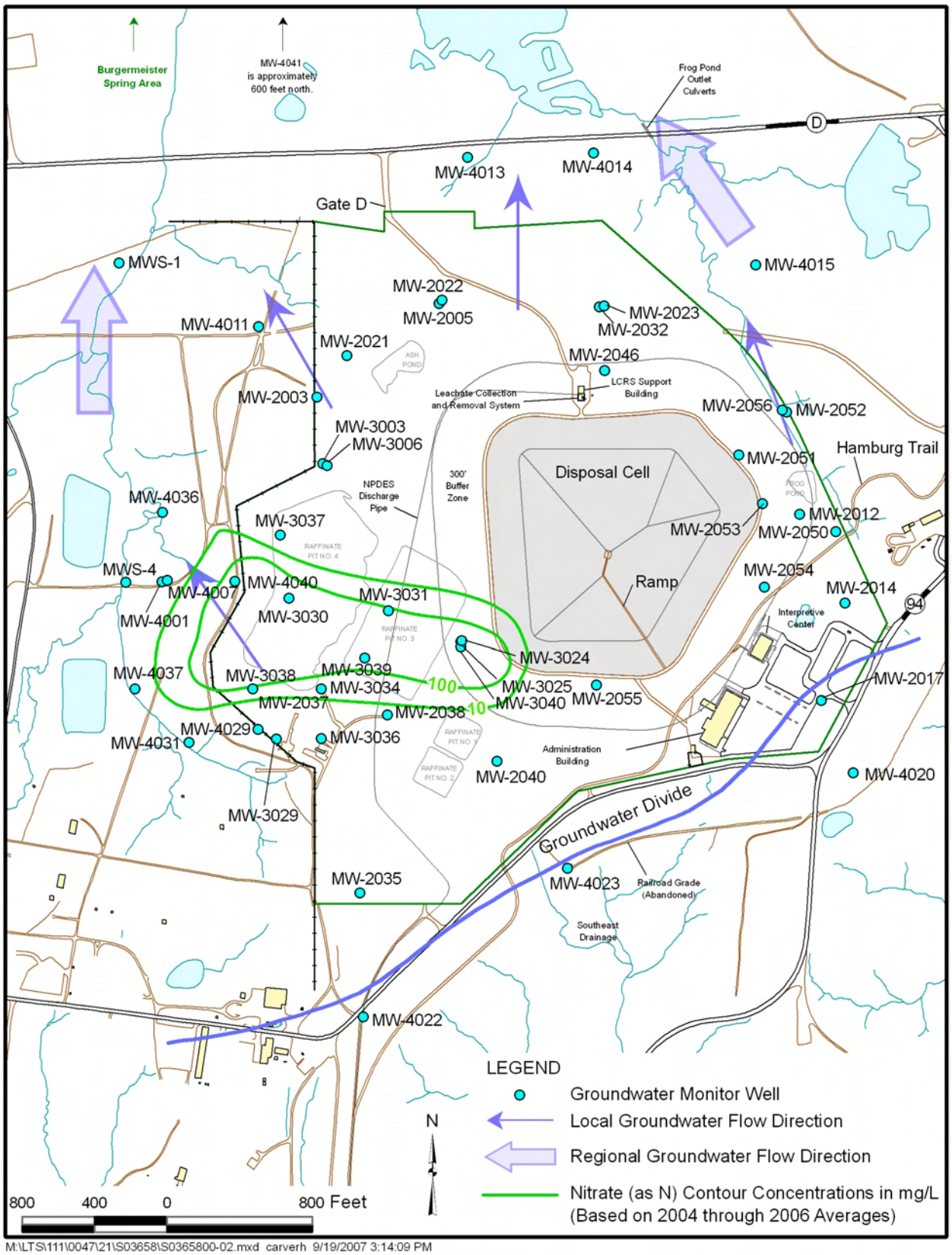

Figure 3–2. Distribution of Nitrate (as N)—Unweathered Unit—MNA Baseline Data (2004−2006)

Table 3–1. Summary of Nitrate (as N) Data from Objective 2 Wells (2004−2006)

Location	Nitrate (as N) Concentrations (mg/L)									
	2004		2005				2006			Average
Weathered Unit										
MW-2038	481		447		528		505		R	498
MW-2040	142		96.9		114		90.3		96.9	108
MW-3003	423		403		435		337		516	392
MW-3034	773		657		505		473		R	602
MW-4013	286		83.8		92.2		88		R	138
MW-4029	537		555		545		515		588	548
MW-4031	174		197		297		162		148	196
MW-4036	26.58		18.6		40.3		9.2		R	23.6
Unweathered Unit										
MW-3040	318	252	222	232	213	215	187	204	192	237
MW-4040	82.2	110	79.5	130	122	138	144	124	65.1	110

R = Data rejected during validation

Nitrate exceeds the MCL in the two unweathered wells located in the raffinate pit area (Table 3–1). The nitrate concentrations in MW-3040 have decreased since installation and have remained stable in MW-4040. Baseline monitoring will continue in these two wells in order to better evaluate changes in concentrations.

The nitrate concentrations in the detection monitoring wells indicate that the movement of the nitrate area of impact is behaving as expected. No increases were observed in either the weathered or unweathered unit wells (Table 3–2). None of these locations exceeds the MCL for nitrate (as N) with the exception of MWS-1, which has consistently exceeded the MCL. The trigger levels set for these locations were not exceeded.

Table 3–2. Summary of Nitrate (as N) Data for Objective 3, 4, and 5 Locations (2004–2006)

Sample ID	Location	Average (mg/L)	Number of Samples
Weathered Unit			
MW-4014	Fringe	6.8	5
MW-4041	Downgradient	0.14	9
MWS-1	Downgradient	11.7	9
MWS-4	Downgradient	2.2	9
Unweathered Unit			
MW-2021	Vertical Extent	ND	5
MW-2022	Vertical Extent	ND	8
MW-3006	Fringe	ND	5
MW-4007	Downgradient	ND	5
MWD-2	Downgradient	ND	8
Springs			
SP-6301	Burgermeister Spring Branch	2.8	5
SP-6303	Burgermeister Spring Branch	5.1	4

The nitrate concentrations in Burgermeister Spring and SP-6303 are less than the MCL of 10 mg/L. The overall trend of nitrate at these locations has been downward.

3.2.2 Uranium

The area of uranium impact is located in the former raffinate pit area (Figure 3−3 and Figure 3−4). Uranium levels exceed the MCL of 20 pCi/L in both the weathered and unweathered units of the Burlington-Keokuk Limestone.

The highest uranium impact in the weathered unit is measured in MW-3024 (Table 3–3). This well has shown variable uranium levels over time. The remaining Objective 2 wells show gradually decreasing uranium levels over the baseline monitoring period. The levels in MW-3003 have consistently been less than the MCL since 2000.

Table 3–3. Summary of Uranium Data from Objective 2 Wells (2004−2006)

Location	Uranium Levels (pCi/L)									
	2004		2005				2006			Average
Weathered Unit										
MW-3003	1.0		1.1		1.2		5.9		0.81	2.0
MW-3024	32.6		61.2		71.1		76.5		67.0	61.7
MW-3030	44.1		45.3		47.6		39.3		41.3	43.5
Unweathered Unit										
MW-3040	94.8	79.9	82.6	90.7	78.5	96.8	86.7	90.0	104	89.4
MW-4040	180	154	175	216	171	255	249	280	236	212

Uranium impact is greatest in the two unweathered wells that were installed beneath and immediately downgradient of the former raffinate pits. These wells were initially installed to be Objective 4 wells; however, uranium levels greater than the MCL were identified. The uranium levels in both of these wells have not stabilized since installation in 2004. The level in MW-4040, which is located downgradient of the area of impact in the weathered unit, has shown an upward trend in uranium levels since installation. Baseline monitoring will continue in these two wells in order to better evaluate changes in concentrations.

Uranium levels in the detection monitoring network indicate that the migration of the area of uranium impact is behaving as expected (Table 3–4). Uranium has increased slightly in MW-4036, which is located immediately downgradient of the area of uranium impact. A maximum of 45 pCi/L has been reported at this location (which is less than the trigger level of 50 pCi/L). Although this level is high, increases are not expected to occur at this downgradient location. No increases were identified in the wells screened in the unweathered unit.

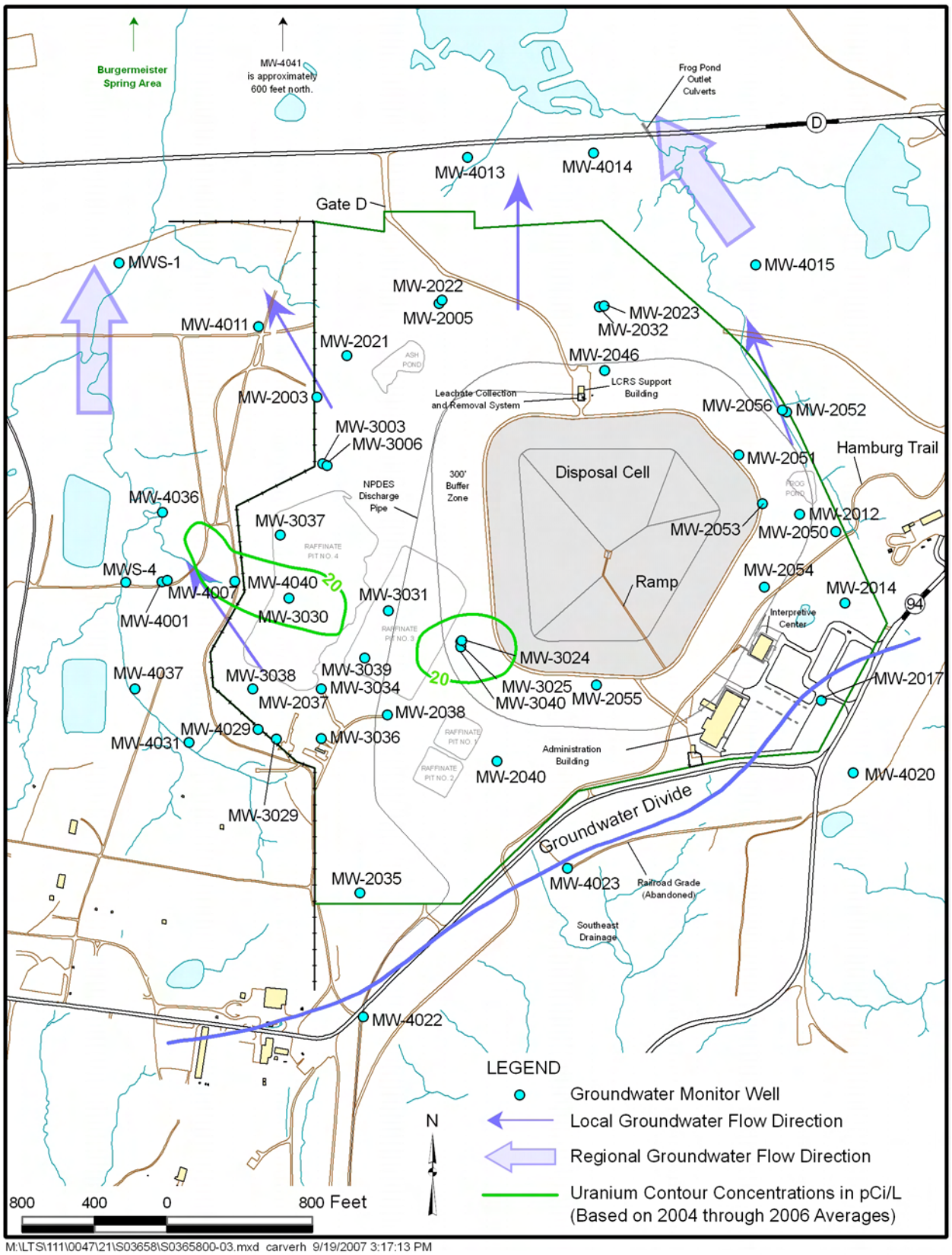

Figure 3–3. Distribution of Uranium—Weathered Unit—MNA Baseline Data (2004−2006)

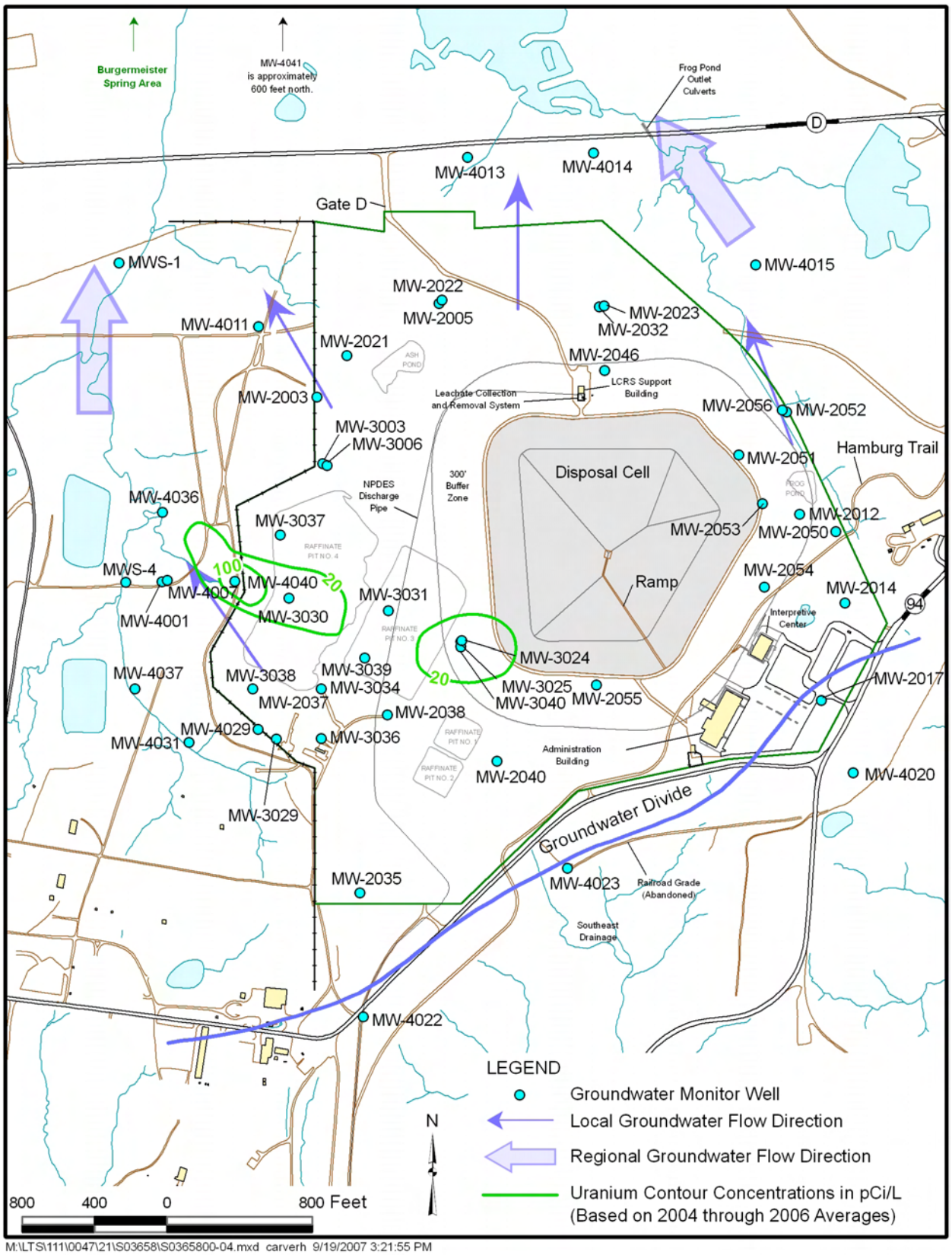

Figure 3–4. Distribution of Uranium—Unweathered Unit—MNA Baseline Data (2004−2006)

Table 3–4. Summary of Uranium Data for Objective 3, 4, and 5 Locations (2004−2006)

Sample ID	Location	Average (pCi/L)	Number of Samples
Weathered Unit			
MW-3031	Fringe	2.4	5
MW-3037	Fringe	2.1	5
MW-4026	Southeast Drainage (alluvium)	ND	5
MW-4036	Downgradient	10.9	5
MW-4041	Downgradient	1.7	9
MWS-1	Downgradient	0.82	9
MWS-4	Downgradient	0.37	9
Unweathered Unit			
MW-3006	Fringe	2.2	4
MWD-2	Downgradient	0.19	8
Springs and Surface Water			
SP-5303	Southeast Drainage	72	5
SP-5304	Southeast Drainage	75	5
SP-6301	Burgermeister Spring Branch	44	5
SP-6303	Burgermeister Spring Branch	1.3	5
SW-2007	Dardenne Creek	0.74	7

Uranium levels in Burgermeister Spring (SP-6301) have increased during the baseline monitoring period; however, these levels are significantly less than historical highs. The levels in Burgermeister Spring exceed the MCL, but they are less than the trigger levels established for the springs. Uranium levels in SP-6303 remain stable and below the MCL.

The uranium levels in the two Southeast Drainage springs monitored under this program have fluctuated over time, and the behavior is similar in both springs. The levels in 2006 are less than those observed in 2005. Uranium levels in both wells exceed the MCL, but they are less than the trigger levels established for the springs.

The uranium levels in Dardenne Creek measured at location SW-2007 are less than the MCL. The levels measured during 2006 are similar to those measured during 2005.

3.2.3 TCE

TCE contamination in the shallow groundwater is located in the vicinity of raffinate pit 4 (Figure 3–5), where drums containing TCE are suspected to have been discarded. TCE impact is detected in only the weathered unit of the Burlington-Keokuk Limestone. TCE levels exceed the MCL of 5 µg/L in the groundwater.

TCE impact is highest in MW-4029 located along a preferential flow pathway in the area (Table 3–5). Concentrations have remained relatively stable during the baseline monitoring period at this location. The TCE concentrations in MW-3030 and MW-3034 appear to have shown an increase during the beginning of the baseline monitoring period; however, this increase is a result of rebound from field studies performed in 2001 and 2002. Recent concentrations appear to have stabilized.

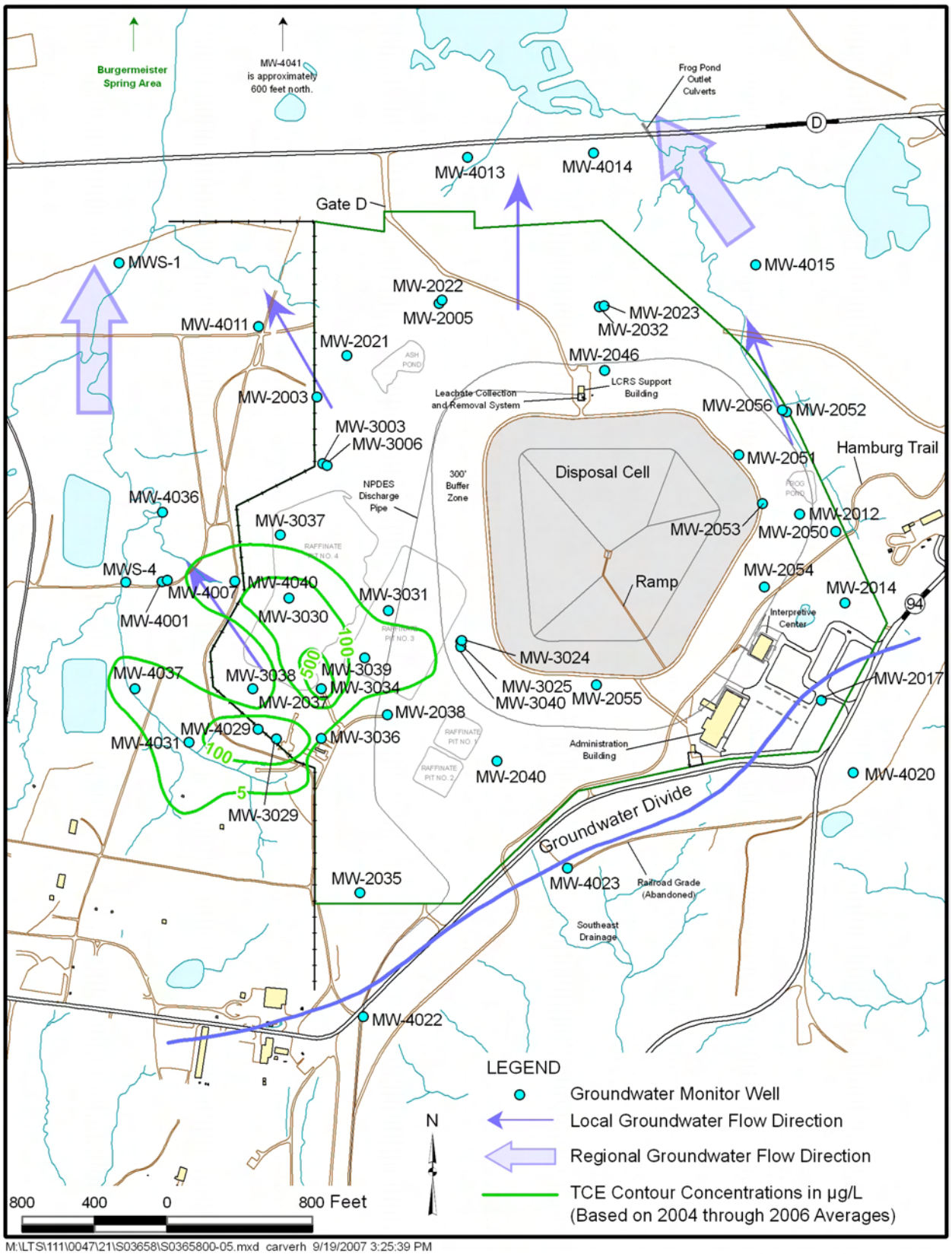

Figure 3–5. Distribution of TCE— Weathered Unit—MNA Baseline Data (2004−2006)

Table 3–5. Summary of TCE Data from Objective 2 Wells (2004−2006)

Location	TCE Concentrations (µg/L)					
	2004	2005		2006		Average
MW-3030	330	420	490	410	380	406
MW-3034	610	580	510	430	430	512
MW-4029	460	490	560	640	560	542

No detectable concentrations of TCE have been reported for the detection monitoring well screen in either the weathered or unweathered units (Table 3–6). This indicates that the area of TCE impact has not expanded laterally or vertically.

Table 3–6. Summary of TCE Data for Objective 3, 4, and 5 Locations (2004−2006)

Sample ID	Location	Average (µg/L)	Number of Samples
Weathered Unit			
MW-3031	Fringe	< 1	5
MW-3037	Fringe	< 1	5
MW-4036	Downgradient	< 1	5
MW-4041	Downgradient	< 1	9
MWS-1	Downgradient	< 1	9
MWS-4	Downgradient	< 1	9
Unweathered Unit			
MW-3006	Fringe	< 1	5
MW-4007	Downgradient	< 1	5
MW-4040	Vertical Extent	< 1	9
Springs			
SP-6301	Burgermeister Spring Branch	< 1	5
SP-6303	Burgermeister Spring Branch	< 1	5

3.2.4 2,4-Dinitrotoluene

Groundwater impacted by 2,4-DNT that exceeds the cleanup standard of 0.11 µg/L is located in the Frog Pond and raffinate pit areas of the chemical plant (Figure 3–6). TNT production lines were located in both of these areas. Nitroaromatic compound impact is isolated to the weathered unit of the Burlington-Keokuk Limestone.

In 2004, a subsidence feature associated with historical trenching activities formed near MW-2012. During that time, the concentrations of nitroaromatic compounds decreased dramatically (DOE 2007). Surface runoff infiltrated the subsurface through this subsidence feature, resulting in the dilution of contaminated groundwater in the vicinity of MW-2012 and other downgradient locations. Data collected subsequent to the repair of the feature in 2006 have shown an increase in nitroaromatic compound concentrations. Downward trends associated with MW-2012 and other nearby wells are not considered to be the result of attenuation processes.

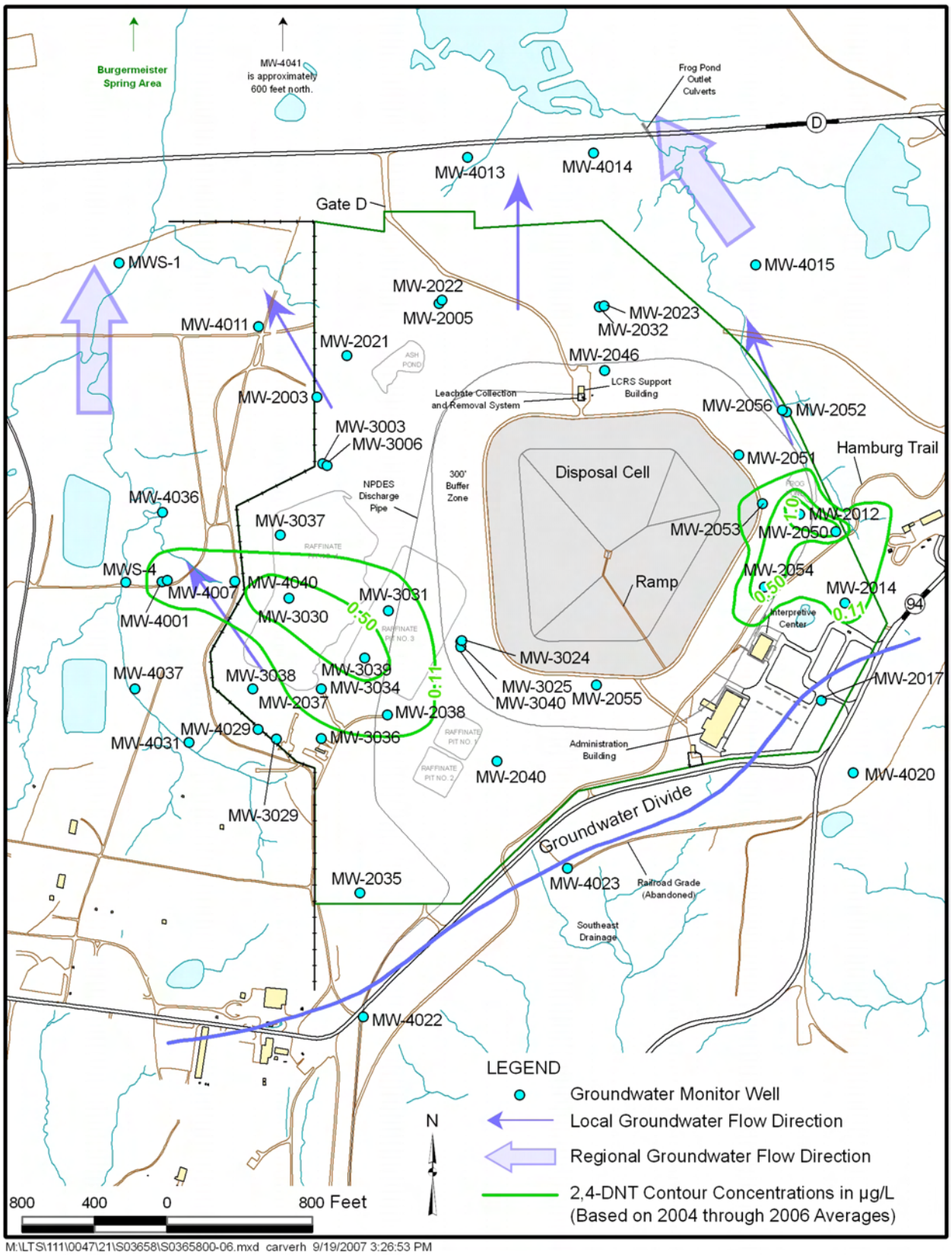

Figure 3–6. Distribution of 2,4-DNT—Weathered Unit—MNA Baseline Data (2004–2006)

The highest 2,4-DNT impact has been associated with MW-2012 (the Frog Pond area) (Table 3–7). Data from the baseline monitoring period have been affected by surface infiltration, resulting in a decrease in 2,4-DNT concentrations at this location. Levels at this location still exceed the cleanup standard of 0.11 µg/L.

Table 3–7. Summary of 2,4-DNT Data from Objective 2 Wells (2004−2006)

Location	2,4-DNT Concentrations (µg/L)					
	2004	2005		2006		Average
Frog Pond Area						
MW-2012	960	1000	830	25	420	543
MW-2014	0.21	0.097	ND	0.12	0.17	0.12
MW-2050	44	46	35	44	41	42
MW-2052	ND	R	ND	ND	0.073	< 0.06
MW-2053	ND	0.23	0.30	0.31	R	0.22
MW-2054	3.5	0.091	ND	ND	1.6	1.0
Raffinate Pit Area						
MW-2038	0.17	0.14	ND	0.21	0.28	0.17
MW-3030	0.98	0.82	0.99	0.93	0.93	0.93
MW-3034	0.42	0.26	ND	0.20	0.20	0.22
MW-3039	1.2	0.6	0.53	0.42	0.38	0.63

R = Data rejected during validation

Concentrations in MW-2050 indicate an increase in 2,4-DNT, though data from the last few years indicates that these concentrations may be stabilizing. Concentrations in MW-2053 also seem to have increased slightly over the last few years. The substantial decrease in MW-2054 is not explained. This well is located upgradient of the subsidence feature close to MW-2012. Data from 2006 indicates that concentrations are increased from those measured in 2005. The other monitoring locations have stable concentrations over time

Elevated concentrations of 2,4-DNT are also present in the former raffinate pit area. Production lines 3 and 4 were located in this area of the site, though production line 4 was primarily on the neighboring Army property. Concentrations of 2,4-DNT continue to exceed the cleanup standard of 0.11 µg/L in this area. Concentrations over time have been relatively stable.

The nitroaromatic compound concentrations in the detection monitoring wells indicate that the movement of the discrete areas of impact is behaving as expected (Table 3–8). No increases were observed in the wells monitoring the weathered unit. The data for the unweathered unit wells were all reported as “not detected.” None of these locations exceeds the cleanup standards for 2,4-DNT or the trigger levels set for these locations.

Table 3–8. Nitroaromatic Compound Data for Objective 3, 4, and 5 Locations (2004−2006)

Sample ID	Location	1,3-DNB	2,4,6-TNT	2,4-DNT	2,6-DNT	NB	Number of Samples
Weathered Unit							
MW-2032	Fringe	ND	ND	ND	ND	ND	2
MW-2051	Fringe	0.08	0.11	0.05	0.07	ND	2
MW-3037	Fringe	---	---	ND	---	---	2
MW-4013	Downgradient	---	---	ND	0.61	ND	2
MW-4014	Downgradient	ND	ND	ND	ND	ND	2
MW-4015	Downgradient	---	---	0.06	0.80	ND	2
MW-4036	Downgradient	---	---	ND	---	---	2
MW-4039	Fringe	ND	ND	ND	ND	ND	2
MW-4041	Downgradient	ND	ND	ND	ND	ND	2
MWS-1	Downgradient	---	---	ND	---	---	2
Unweathered Unit							
MW-2022	Fringe	ND	ND	---	---	---	3
MW-2023	Vertical Extent	ND	ND	ND	ND	ND	3
MW-2056	Vertical Extent	ND	ND	ND	ND	ND	3
MW-3006	Fringe	---	---	ND	---	---	2
MW-4040	Vertical Extent	---	---	ND	---	---	3
Springs							
SP-6301	Burgermeister Spring Branch	ND	ND	ND	ND	ND	5
SP-6303	Burgermeister Spring Branch	ND	ND	0.13	0.15	ND	5

3.2.5 2,6-Dinitrotoluene

Groundwater impacted by 2,6-DNT that exceeds the cleanup standard of 1.3 µg/L is located in a discrete portion of the Frog Pond area (Figure 3–7). Nitroaromatic compound impact is isolated to the weathered unit of the Burlington-Keokuk Limestone.

Concentrations of 2,6-DNT have been the highest in MW-2012 but have shown a substantial decrease since 2004 (Table 3–9). The behavior of the concentrations over time for 2,6-DNT in this well and others are similar to those for 2,4-DNT and are suspected to be affected by surface infiltration since 2004 (DOE 2007). Increased concentrations are observed in MW-2054. The increases observed during the second sampling period may be a result of the 2006 elimination of the infiltration. Concentrations in MW-2014 and MW-2052 are relatively stable.

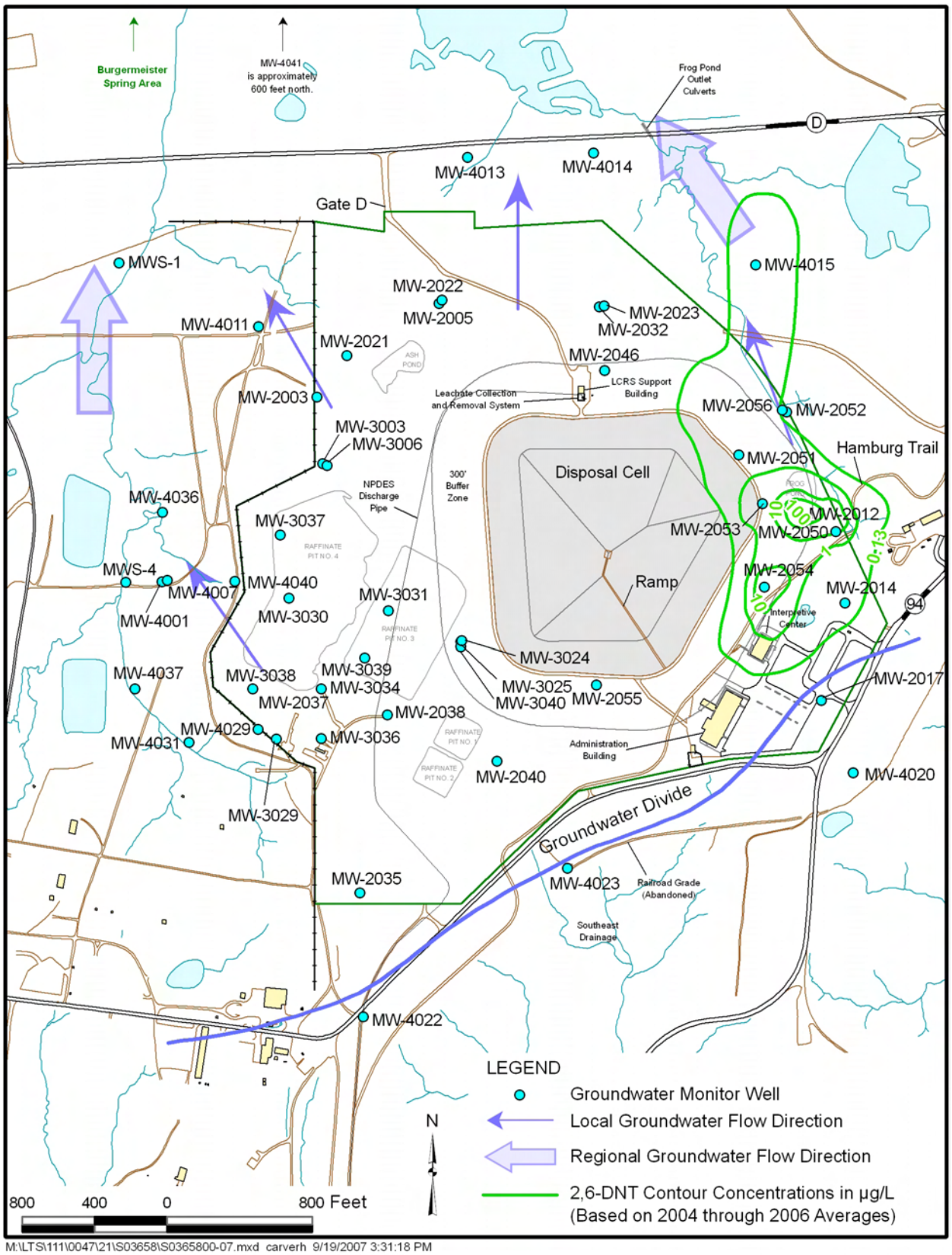

Figure 3–7. Distribution of 2,6-DNT—Weathered Unit—MNA Baseline Data (2004–2006)

Table 3–9. Summary of 2,6-DNT Data from Objective 2 Wells (2004−2006)

Location	2,6-DNT Concentrations (µg/L)					
	2004	2005		2006		Average
MW-2012	750	730	650	66	370	439
MW-2014	0.51	0.42	0.53	0.46	0.60	0.50
MW-2050	33	36	43	49	48	42
MW-2052	ND	0.97	ND	ND	0.23	0.26
MW-2053	3.9	4.8	4.4	5.1	4.9	4.6
MW-2054	48	1.1	0.99	ND	26	15

The nitroaromatic compound concentrations in the detection monitoring wells indicate that the movement of the discrete areas of impact is behaving as expected (Table 3–8). No increases were observed in the wells monitoring the weathered unit. The data for the unweathered unit wells were all reported as "not detected." None of these locations exceeds the cleanup standards for 2,6-DNT or the trigger levels set for these locations.

3.2.6 2,4,6-Trinitrotoluene

Groundwater impacted with 2,4,6-TNT that exceeds the cleanup standard of 2.8 µg/L is located in two discrete portions of the Frog Pond area (Figure 3−8). Nitroaromatic compound impact is isolated to the weathered unit of the Burlington-Keokuk Limestone.

The highest TNT concentrations are associated with MW-2012 (Table 3–10). Data collected since 2004 has indicated a substantial decrease, which is suspected to be associated with surface infiltration (DOE 2007). It appears that this surface infiltration may have also affected concentrations in well MW-2053, based on the similar behavior of contaminant concentrations since 2004. During 2005, the concentrations in MW-2046 also decreased.

Table 3–10. Summary of 2,4,6-TNT Data from Objective 2 Wells (2004−2006)

Location	2,4,6-DNT Concentrations (µg/L)					
	2004	2005		2006		Average
MW-2012	130	67	22	3.4	R	56
MW-2046	R	1.2	ND	1.1	4.8	1.8
MW-2053	ND	2.6	ND	ND	R	0.67

R = Data rejected during validation

The nitroaromatic compound concentrations in the detection monitoring wells indicate that the movement of the discrete areas of impact is behaving as expected (Table 3–8). No increases were observed in the weathered unit wells. The data for the unweathered unit wells were all reported as "not detected." None of these locations exceeds the cleanup standards for 2,4,6-TNT or the trigger levels set for these locations.

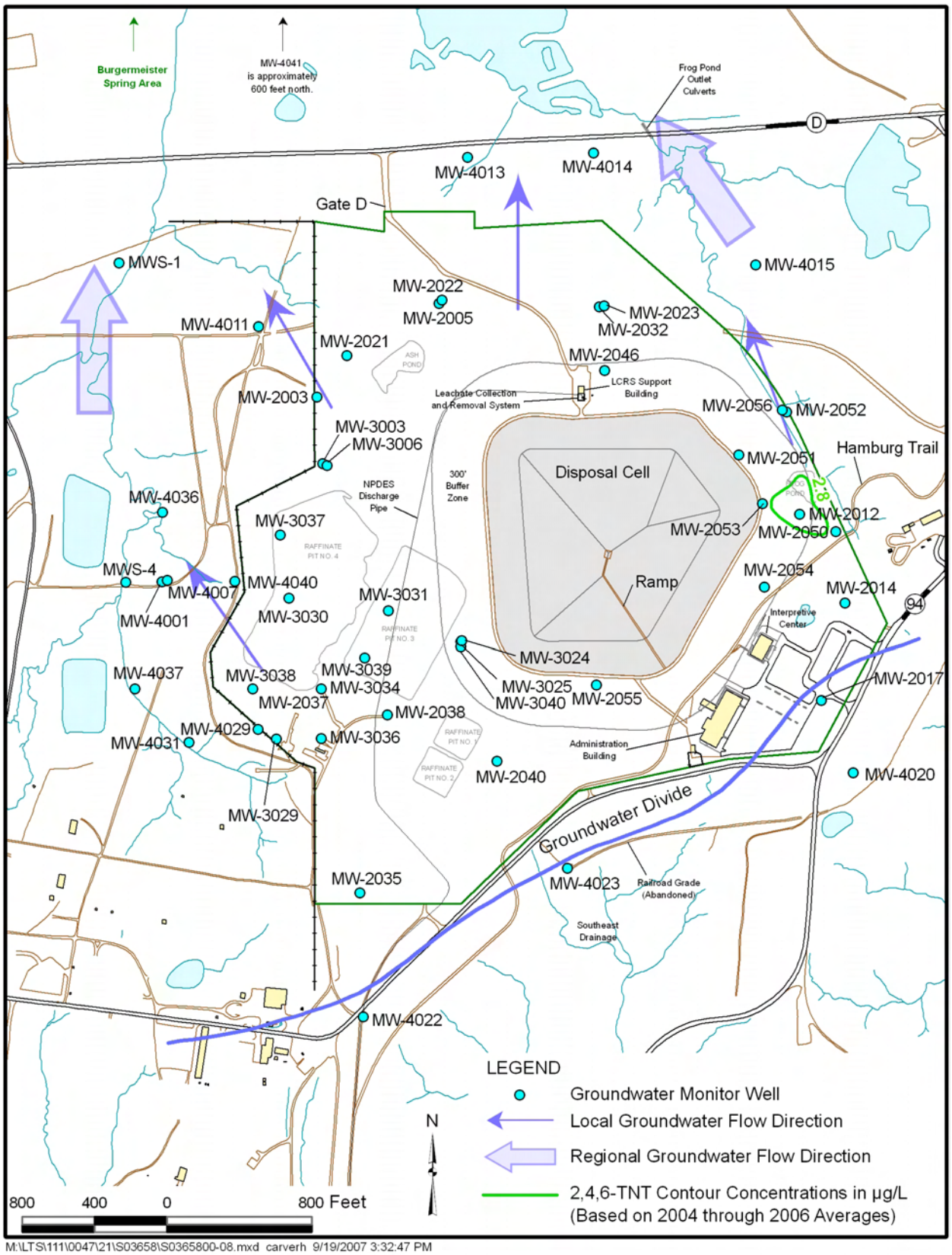

Figure 3–8. Distribution of 2,4,6-TNT—Weathered Unit—MNA Baseline Data (2004−2006)

3.2.7 1,3-Dinitrobenzene

Groundwater impacted by 1,3-DNB is located in a discrete portion of the Frog Pond area, where a TNT production line was located. Nitroaromatic compound impact is isolated to the weathered unit of the Burlington-Keokuk Limestone.

Impact from 1,3-DNB is highest in well MW-2012 (Table 3–11). This well is located adjacent to the production houses for TNT Line 1. Concentrations of 1,3-DNB have fluctuated in this well over time. Presently the average concentration has decreased below the cleanup standard of 1.0 µg/L. It is suspected that the decreases in nitroaromatic compounds observed at this location (and others) are the result of surface infiltration.

Table 3–11. Summary of 1,3-TNB Data from Objective 2 Wells (2004−2006)

Location	1,3-TNB Concentrations (µg/L)					
	2004	2005		2006		Average
MW-2012	0.99	0.16	0.60	ND	0.13	0.67

3.2.8 Nitrobenzene

Groundwater impacted by nitrobenzene that exceeded the cleanup standard of 17 µg/L was located in a discrete portion of the Frog Pond area (MW-2012). Nitroaromatic compound impact was isolated to the weathered unit of the Burlington-Keokuk Limestone. Nitrobenzene has not been detected at this location since 2002 when a one-time detection of 69 µg/L was measured. A summary of the data from the baselining period is presented in Table 3–12.

Table 3–12. Summary of Nitrobenzene Data from Objective 2 Wells (2004−2006)

Location	Nitrobenzene Concentrations (µg/L)					
	2004	2005		2006		Average
MW-2012	ND	ND	ND	ND	ND	ND

3.2.9 Background (Objective 1) Data

Baseline conditions are monitored in four wells to evaluate possible changes in downgradient areas of impact. The objective of this monitoring is to determine if baseline conditions remain unchanged. The annual average concentration for each parameter is presented in Table 3–13.

Table 3–13. Summary of Background Monitoring Locations (Objective 1) (2004−2006)

Location	MW-2017	MW-2035	MW-4022	MW-4023
Zone	Weathered	Weathered	Unweathered	Weathered
Number of Samples	5	5	5	5
Parameters				
Uranium (pCi/L)	NA	0.44	3.4	1.9
Nitrate (as N) (mg/L)	NA	0.45	0.26	0.96
TCE (µg/L)	NA	< 1	NA	NA
1,3-DNB (µg/L)	ND	ND	NA	NA
2,4,6-TNT (µg/L)	ND	ND	NA	NA
2,4-DNT (µg/L)	ND	ND	NA	NA
2,6-DNT (µg/L)	ND	ND	NA	NA
Nitrobenzene (µg/L)	ND	ND	NA	NA

ND – Analyte not detected above method detection limit
NA – Analyte not analyzed

3.3 Temporal Trends in Contaminant Concentration

Concentrations of contaminants of concern are expected to decrease to cleanup standards within a reasonable timeframe (i.e., approximately 100 years). Long-term trend analysis is performed to confirm downward trends in contaminant concentrations over time. Performance of the remedy will be gauged against long-term trends in the Objective 2 wells for each COC. Some locations are expected to show temporary upward trends as a result of recent source removal and ongoing dispersion.

Testing for temporal trends was performed for the COCs for the GWOU using data collected between 2002 and 2006. The non-parametric Mann-Kendall test was applied as outlined in the RD/RA Work Plan (DOE 20004b). Results for the trending analysis are reported for the Objective 2 wells and the Objective 5 springs, as these locations monitor the area of groundwater impact and the discharge points.

Graphs of the annual averages over time have been prepared to provide a visual representation of the data. Graphs of the annual averages of COCs at each location can be used to draw a comparison between the results of the trend analysis and the contaminant data. Comparisons of the graphs to the trending results provide support to the occurrence of a trend in the data that might not be identified by only the graph.

3.3.1 Nitrate (as N)

The concentrations of nitrate have stabilized over the past 5 years, and some decreases have been indicated, as shown in Figure 3–9 and Figure 3–10, based on the results of the trending analyses (Table 3–14). No upward trends were calculated. Again, the stabilization of the concentrations is the result of source removal in the raffinate pit and Ash Pond areas.

Table 3–14. Trending Analysis for Nitrate (as N) in Objective 2 MNA Wells

Location	No. of Samples	Trend	Slope	Confidence Intervals	
				Lower	Upper
MW-2038	14	None	-51.896	-106.164	48.496
MW-2040	12	Down	-7.335	-28.711	2.698
MW-3003	13	None	13.259	-39.243	74.141
MW-3034	14	None	0.921	-61.362	94.288
MW-3040	11	Down	-32.401	-59.513	-22.272
MW-4013	8	None	3.910	-26.266	16.828
MW-4029	15	None	12.481	-17.237	45.85
MW-4031	15	Down	-22.455	-44.438	-8.408
MW-4036	7	None	-7.520	-12.447	6.280
MW-4040	11	None	12.986	-22.956	37.920

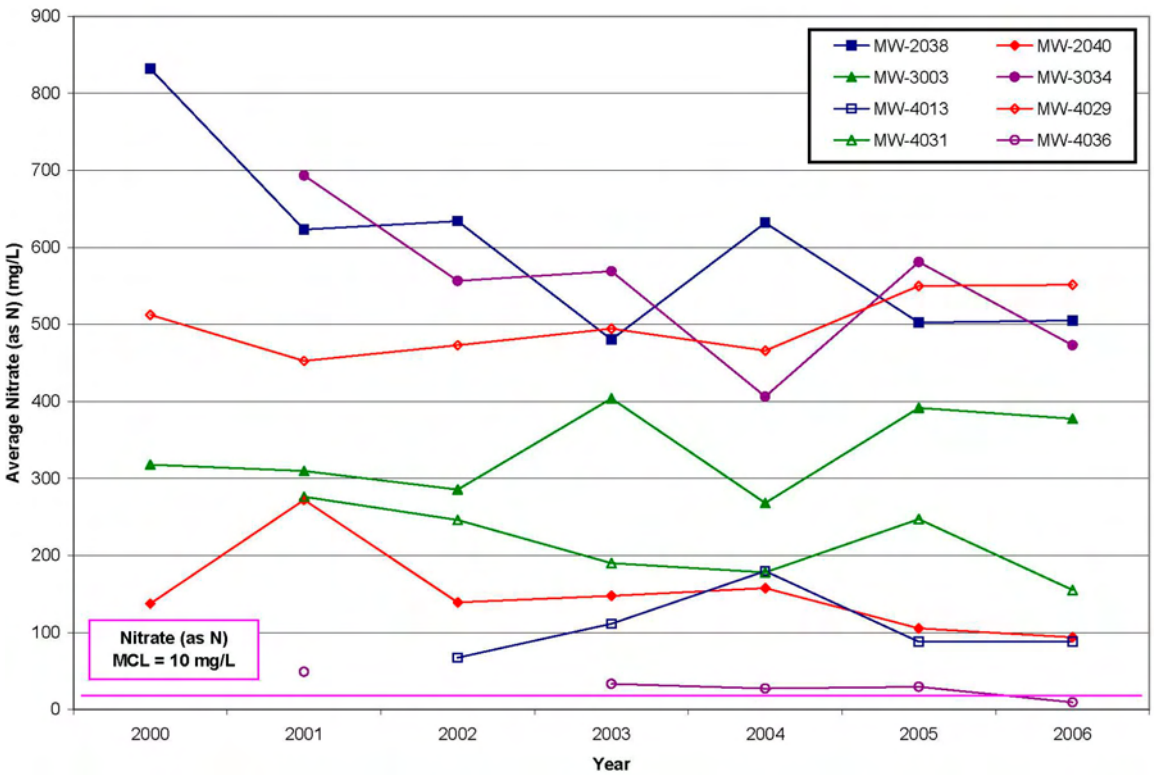

Figure 3–9. Annual Average Nitrate Concentrations in Objective 2 Wells Screened in the Weathered Unit (2000−2006)

Figure 3–10. Annual Average Nitrate Concentrations in Objective 2 Wells Screened in the Unweathered Unit (2004−2006)

3.3.2 Uranium

Results for trend analyses for uranium (Table 3–15) indicate that the levels are either stable or decreasing in all of the Objective 2 wells except for MW-4040. A review of the graphs of the annual uranium averages (Figure 3–11 and Figure 3–12) at each of these locations supports the trend analysis results. The stabilization of the uranium levels is the result of source removal in the raffinate pit area; however, a flushing of the system is slow due to the low amount of recharge through the system. The increases in MW-4040 will continue to be evaluated.

Table 3–15. Trending Analysis for Uranium in Objective 2 MNA Wells

Location	No. of Samples	Trend	Slope (pCi/L/yr)	Confidence Intervals	
				Lower	Upper
MW-3003	12	Down	-2.268	-3.465	-0.788
MW-3024	15	None	4.633	-5.792	14.444
MW-3030	18	Down	-2.609	-3.442	-1.301
MW-3040	11	None	4.133	-5.340	12.710
MW-4040	11	Up	44.724	-3.663	76.256

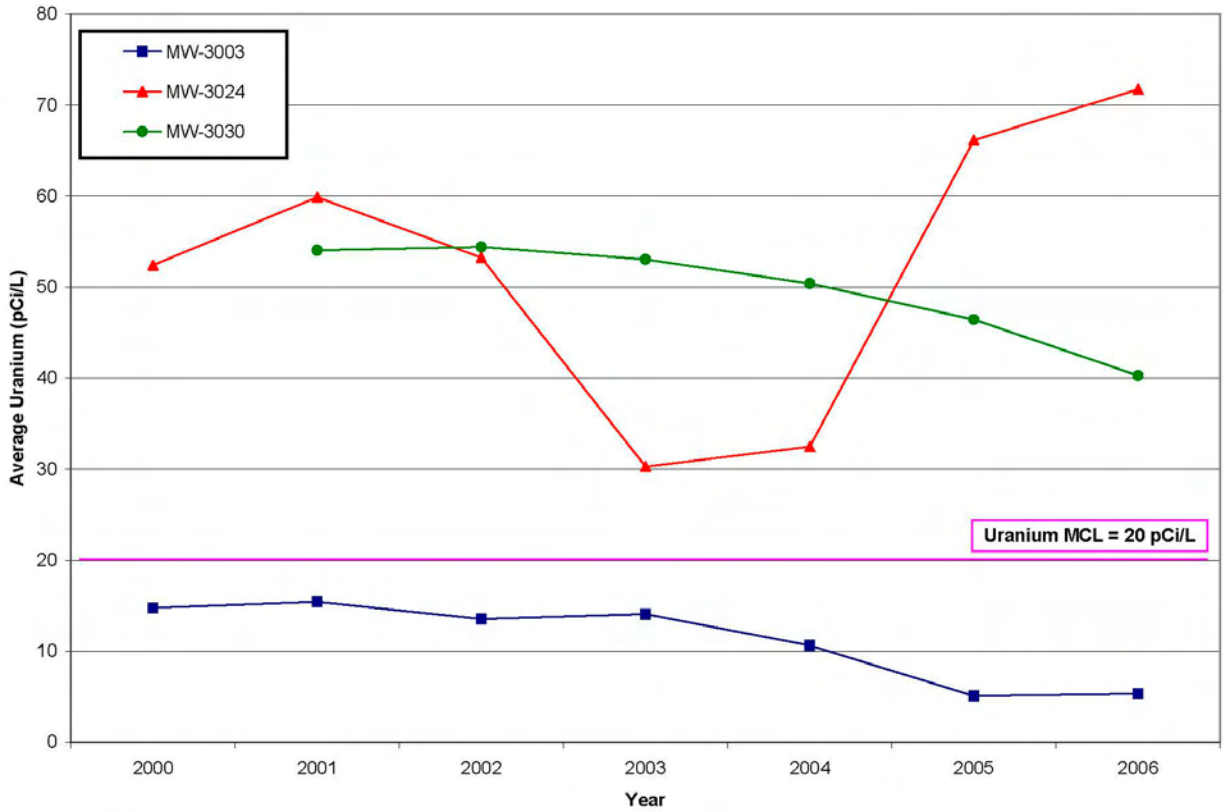

Figure 3–11. Annual Average Uranium Levels in Objective 2 Wells Screened in the Weathered Unit (2000−2006)

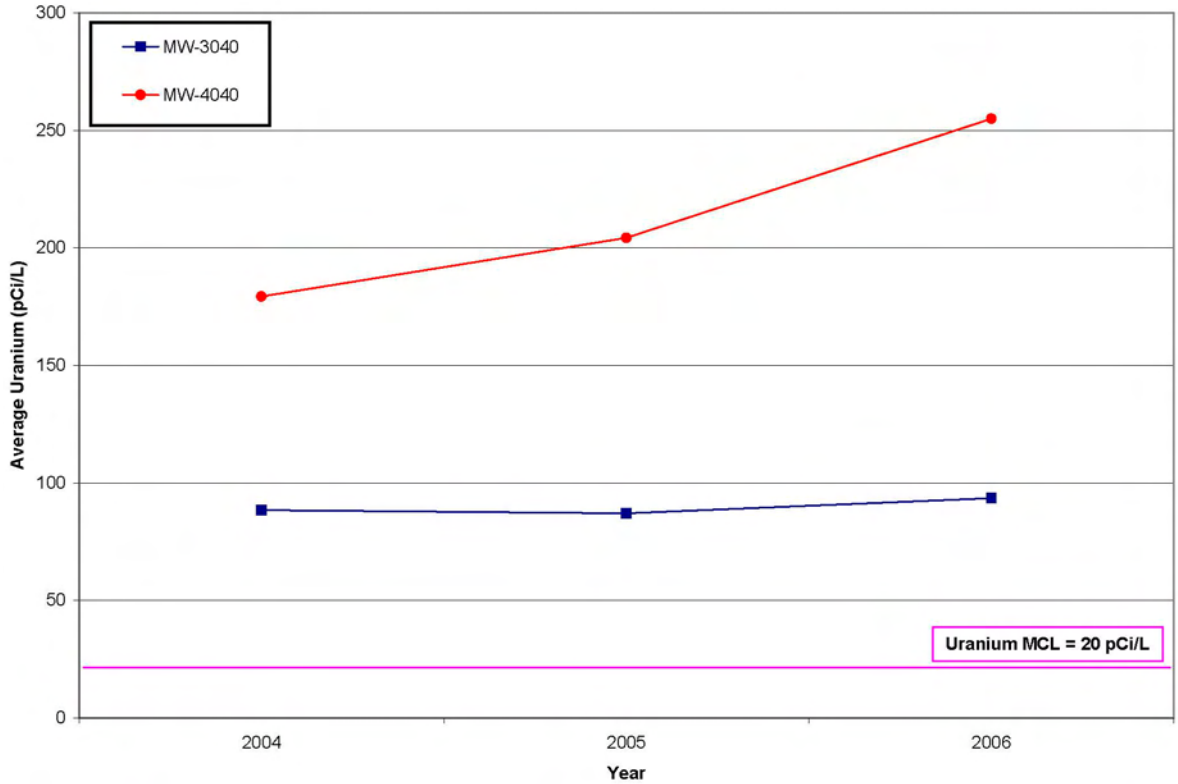

Figure 3–12. Annual Average Uranium Levels in Objective 2 Wells Screened in the Unweathered Unit (2000−2006)

3.3.3 TCE

A review of the annual averages over time (Figure 3−13) and results of the trend analysis for the Objective 2 wells indicates that TCE in groundwater is stable (Table 3–16). An upward trend was determined for MW-3030; however, this location showed the greatest effects of the additional groundwater field studies and the ICO pilot scale study performed in 2001. This well is still rebounding from these studies.

Table 3–16. Trending Analysis for TCE in Objective 2 MNA Wells

Location	No. of Samples	Trend	Slope	Confidence Intervals	
				Lower	Upper
MW-3030	16	Up	49.903	23.090	109.226
MW-3034	18	None	-42.372	-4,570.54	59.156
MW-4029	18	None	22.190	-8.130	61.987

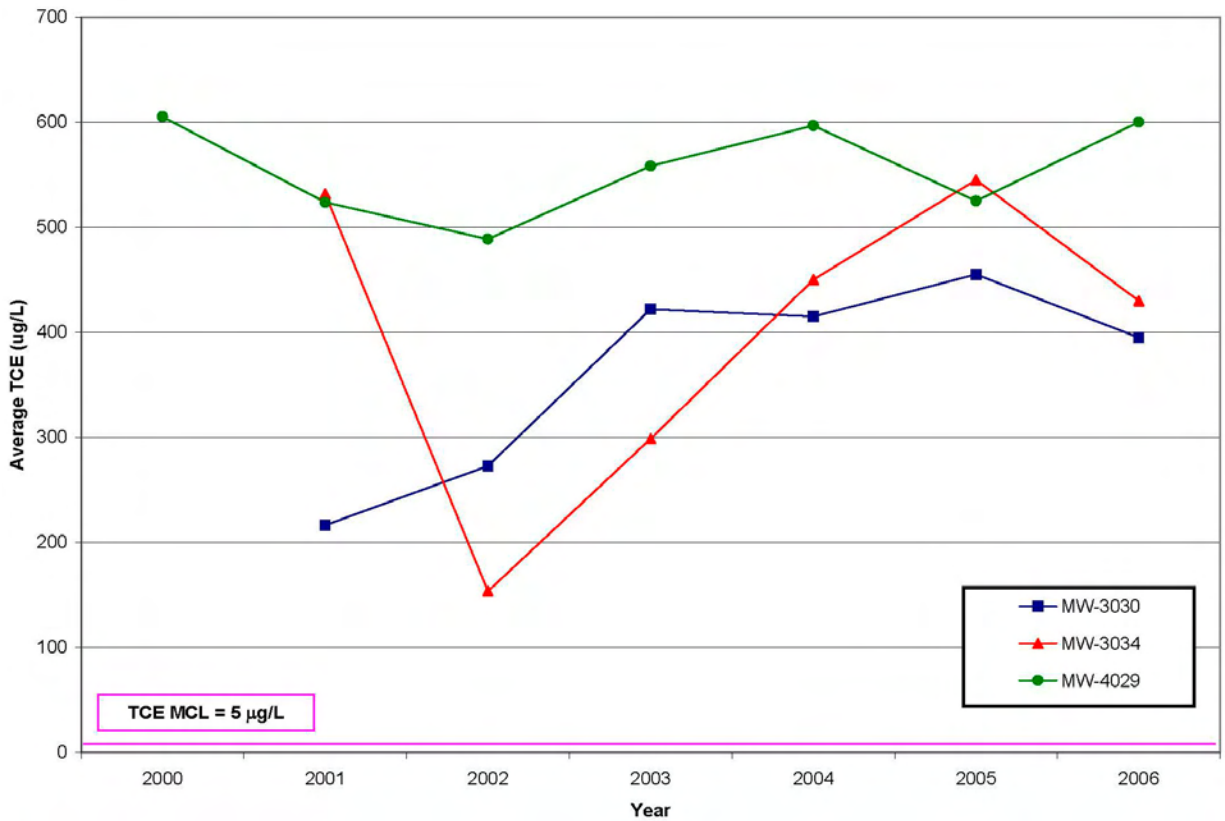

Figure 3–13. Annual Average TCE Concentrations in Objective 2 Wells (2000–2006)

3.3.4 Nitroaromatic Compounds

Results of the trend analyses for the nitroaromatic compounds (Table 3–17 through Table 3–20) indicated upward trends in the Frog Pond area for 2,4,6-TNT, 2,4-DNT, and 2,6-DNT. Wells MW-2050, MW-2052, and MW-2053 showed upward trends for one or more of these nitroaromatic compounds. Decreasing trends in 2,4-DNT were determined for MW-3030 and

MW-3039 in the raffinate pit area. A review of the annual averages over time reflects the upward and downward trends (Figure 3–15 through Figure 3–20).

Table 3–17. Trending Analysis for 2,4-DNT in Objective 2 MNA Wells

Location	No. of Samples	Trend	Slope	Confidence Intervals	
				Lower	Upper
MW-2012	19	Down	-236.021	-330.576	-138.092
MW-2014	16	None	0.008	-0.007	0.035
MW-2038	15	None	-0.002	-0.050	0.067
MW-2046	10	None	182.621	-5856.33	182.621
MW-2050	17	None	1.661	-1.400	5.277
MW-2052	18	Up	182.621	0.014	5375.88
MW-2053	18	None	182.621	-0.020	182.621
MW-2054	18	None	0.414	-1.230	5.721
MW-3030	18	Down	-0.041	-0.078	0.0
MW-3034	18	None	0.010	-0.040	0.076
MW-3039	14	Down	-0.193	-0.379	0.0

Table 3–18. Trending Analysis for 2,6-DNT in Objective 2 MNA Wells

Location	No. of Samples	Trend	Slope	Confidence Intervals	
				Lower	Upper
MW-2012	19	Down	-189.385	-267.798	-103.084
MW-2014	16	None	0.014	-0.040	0.091
MW-2050	17	Up	10.324	8.909	11.562
MW-2052	18	Up	182.621	0.027	5088.54
MW-2053	18	None	0.077	-0.639	0.779
MW-2054	18	None	0.0	-12.567	15.385

Table 3–19. Trending Analysis for 2,4,6-TNT in Objective 2 MNA Wells

Location	No. of Samples	Trend	Slope	Confidence Intervals	
				Lower	Upper
MW-2012	19	Down	-53.113	-77.311	-17.676
MW-2046	11	None	-0.050	-1.216	0.652
MW-2053	18	Up	1.548	0.194	9.772

Table 3–20. Trending Analysis for 1,3-DNB in Objective 2 MNA Wells

Location	No. of Samples	Trend	Slope	Confidence Intervals	
				Lower	Upper
MW-2012	19	None	-0.031	-0.420	0.848

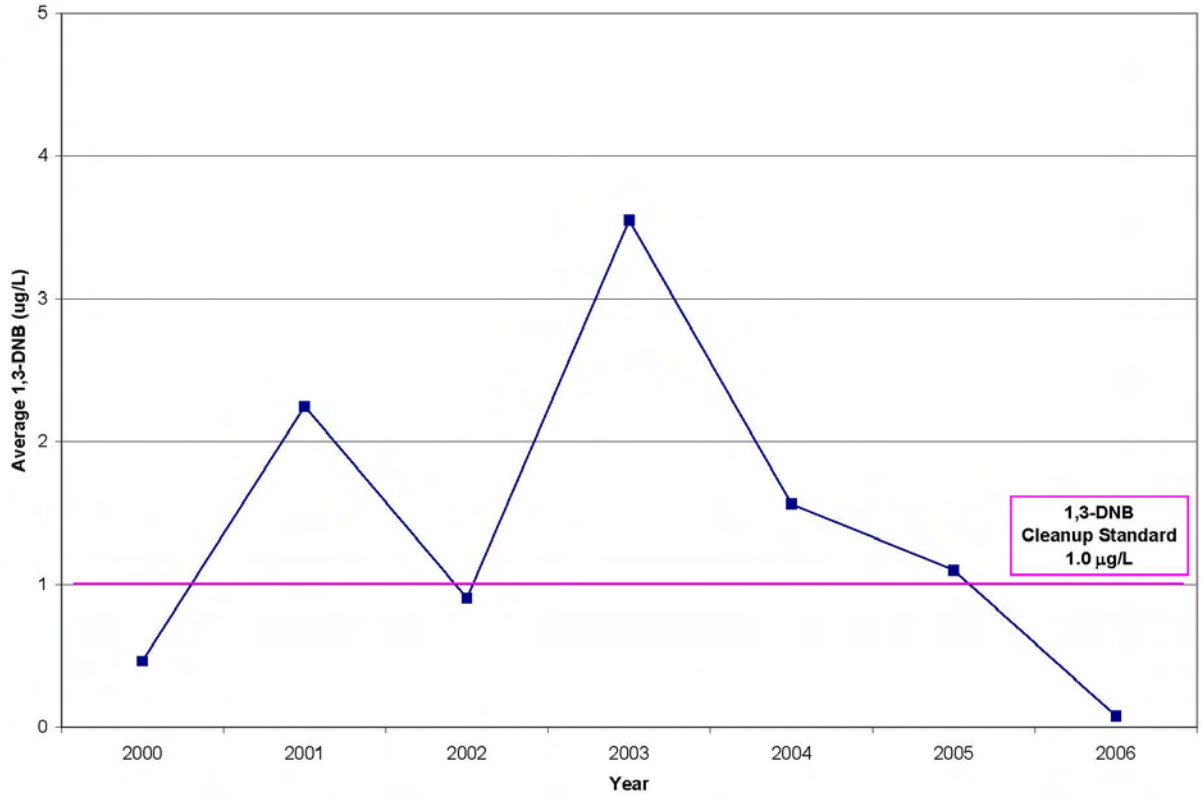

Figure 3–14. Annual Average 1,3-DNB Concentrations in Objective 2 Well MW-2012 (2000−2006)

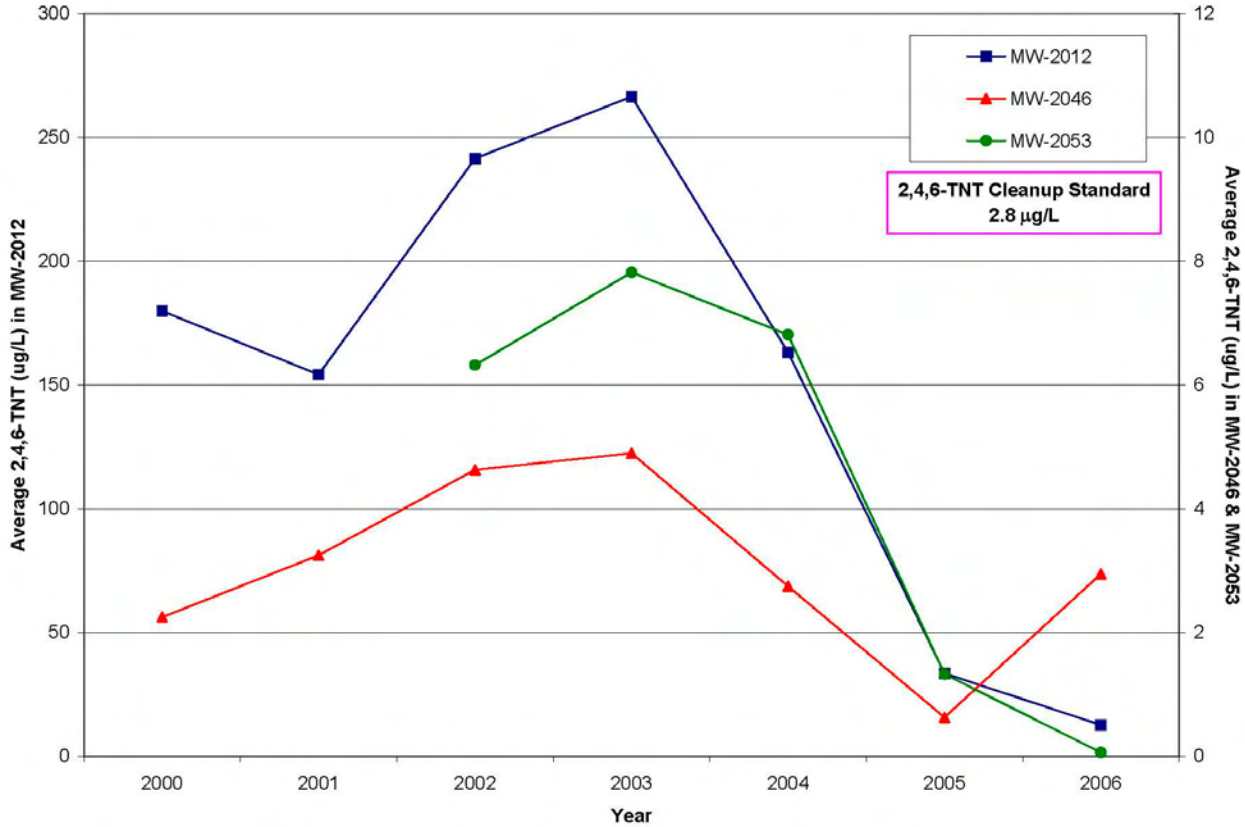

Figure 3–15. Annual Average 2,4,6-TNT Concentrations in Objective 2 Wells (2000−2006)

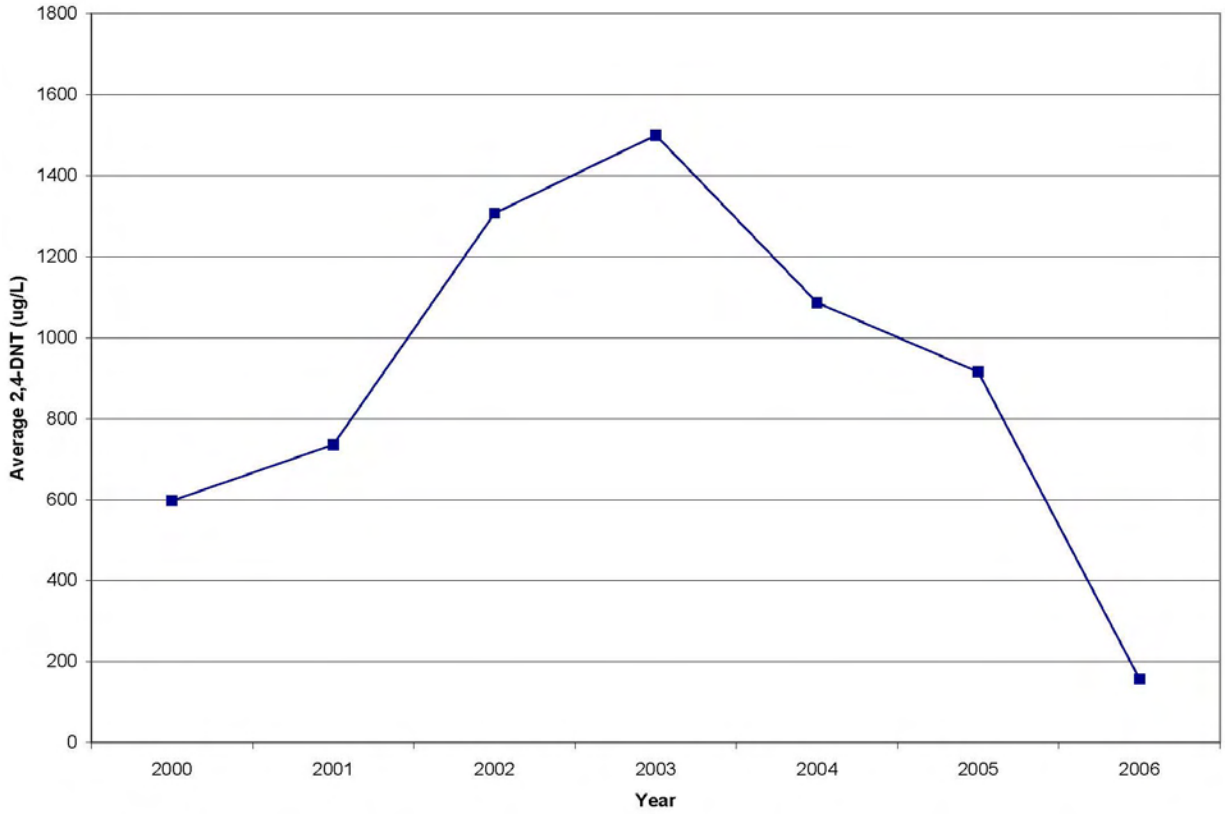

Figure 3–16. Annual Average 2,4-DNT Concentrations in Objective 2 Well MW-2012 (2000−2006)

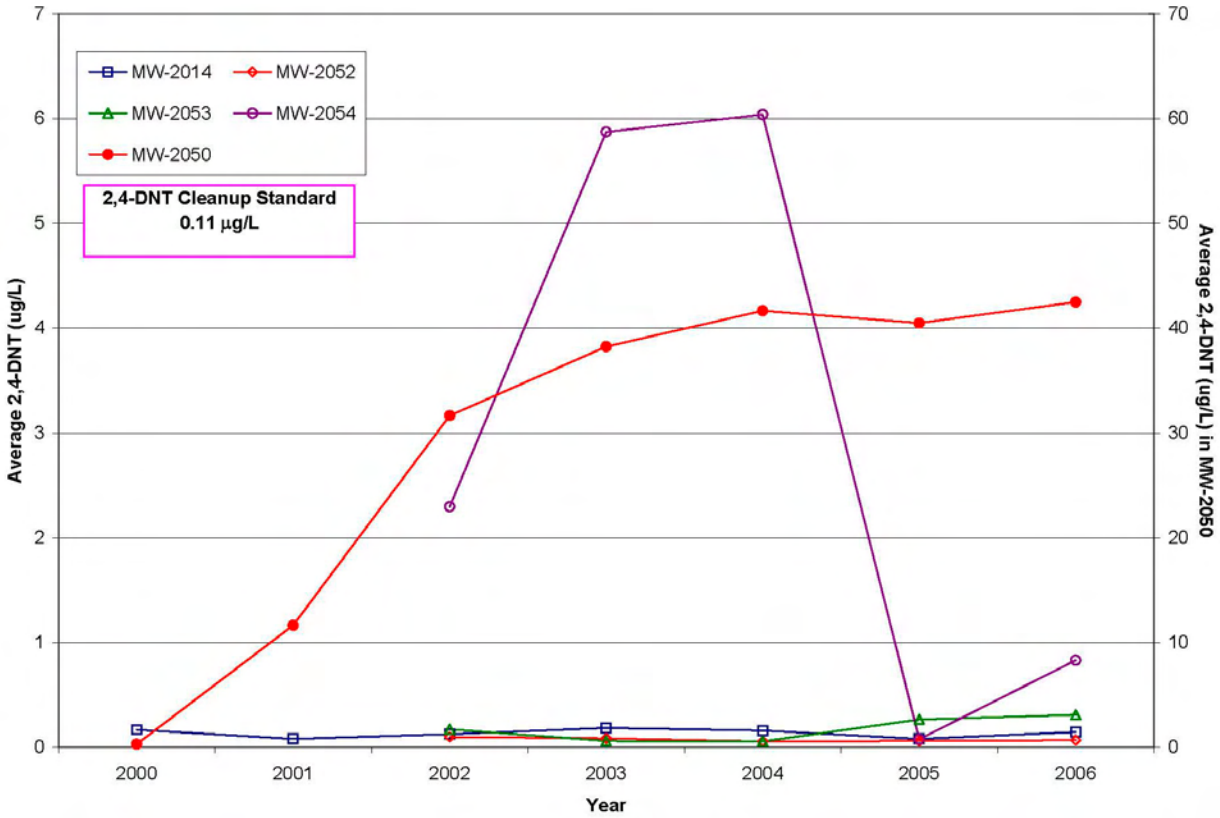

Figure 3–17. Annual Average 2,4-DNT Concentrations in Objective 2 Wells in the Frog Pond Area (2000−2006)

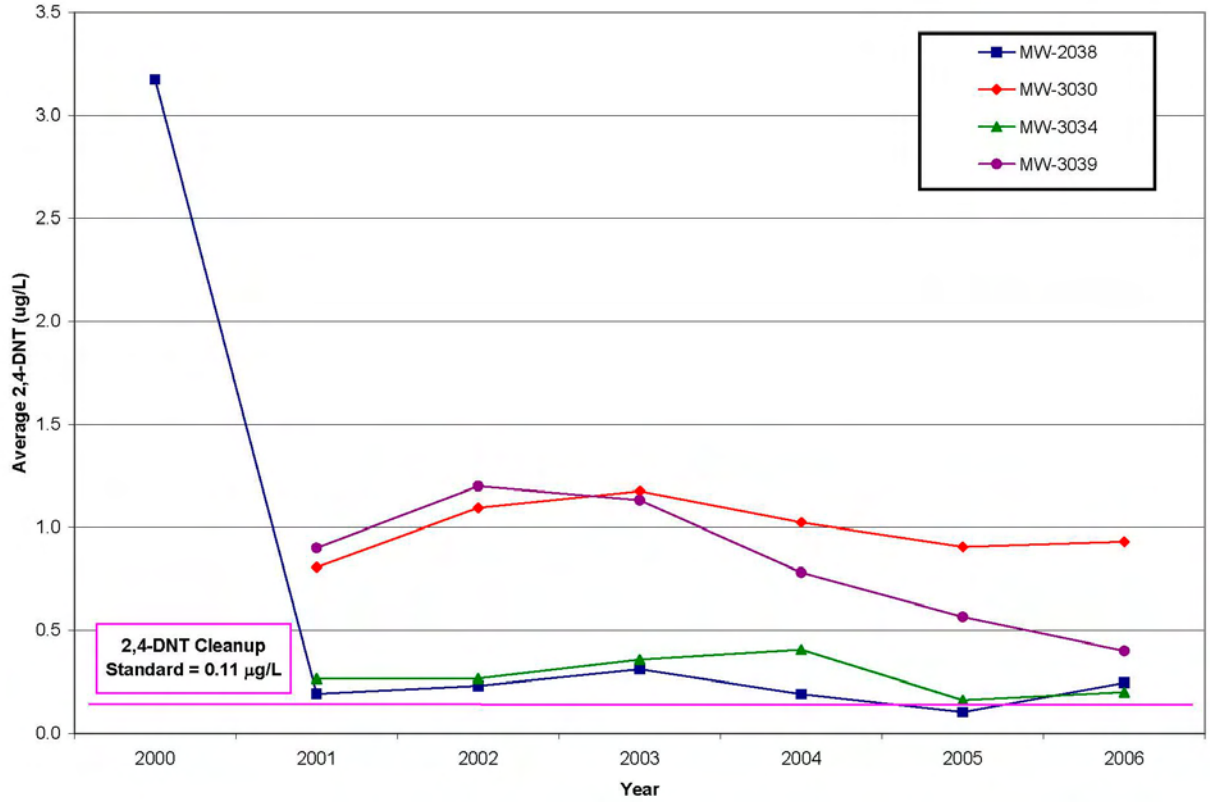

Figure 3–18. Annual Average 2,4-DNT Concentrations in Objective 2 Wells in the Raffinate Pit Area (2000−2006)

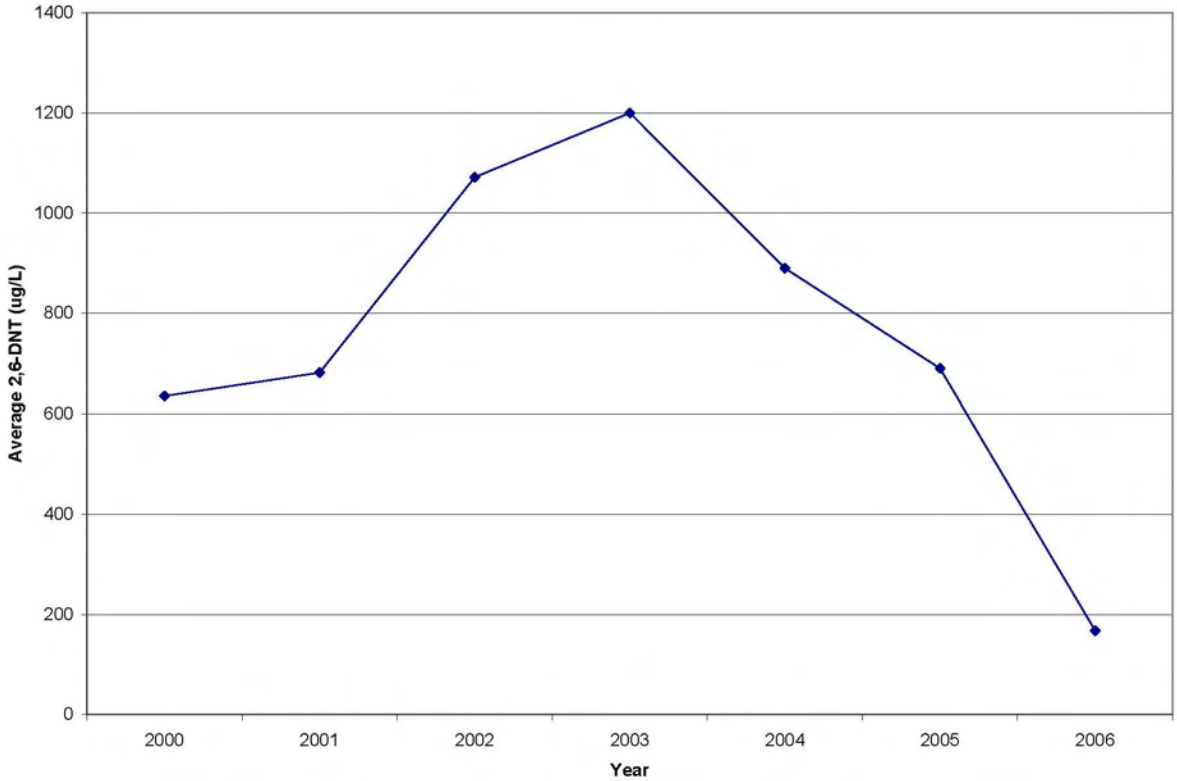

Figure 3–19. Annual Average 2,6-DNT Concentrations in Objective 2 Well MW-2012 (2000−2006)

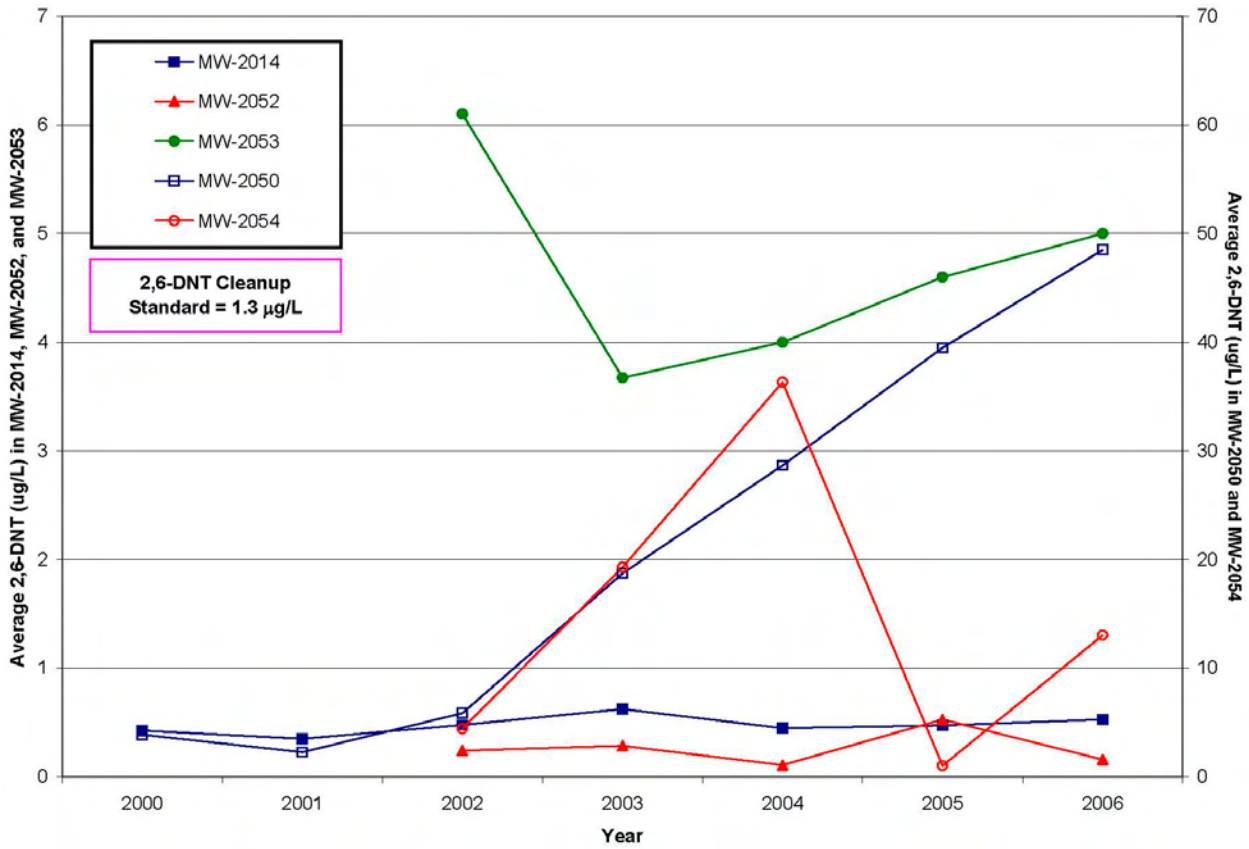

Figure 3–20. Annual Average 2,6-DNT Concentrations in Objective 2 Wells (2000−2006)

Testing for temporal uranium trends during the past 5 years at the Objective 5 springs (Table 3–21) indicated an upward trend at SP-6301 (Burgermeister Spring). The uranium levels at the remainder of the springs were considered stable. This upward trend is reflected in the annual averages over time (Figure 3–21). The levels in the Southeast Drainage springs are stable (Figure 3–22).

Table 3–21. Trending Analysis for Uranium in Objective 5 MNA Springs

Location	No. of Samples	Trend	Slope	Confidence Intervals	
				Lower	Upper
SP-5303	19	None	5.285	-7.143	14.511
SP-5304	24	None	6.478	-1.051	15.153
SP-6301	25	Up	5.099	-0.339	11.467
SP-6303	23	None	0.060	-0.202	0.312

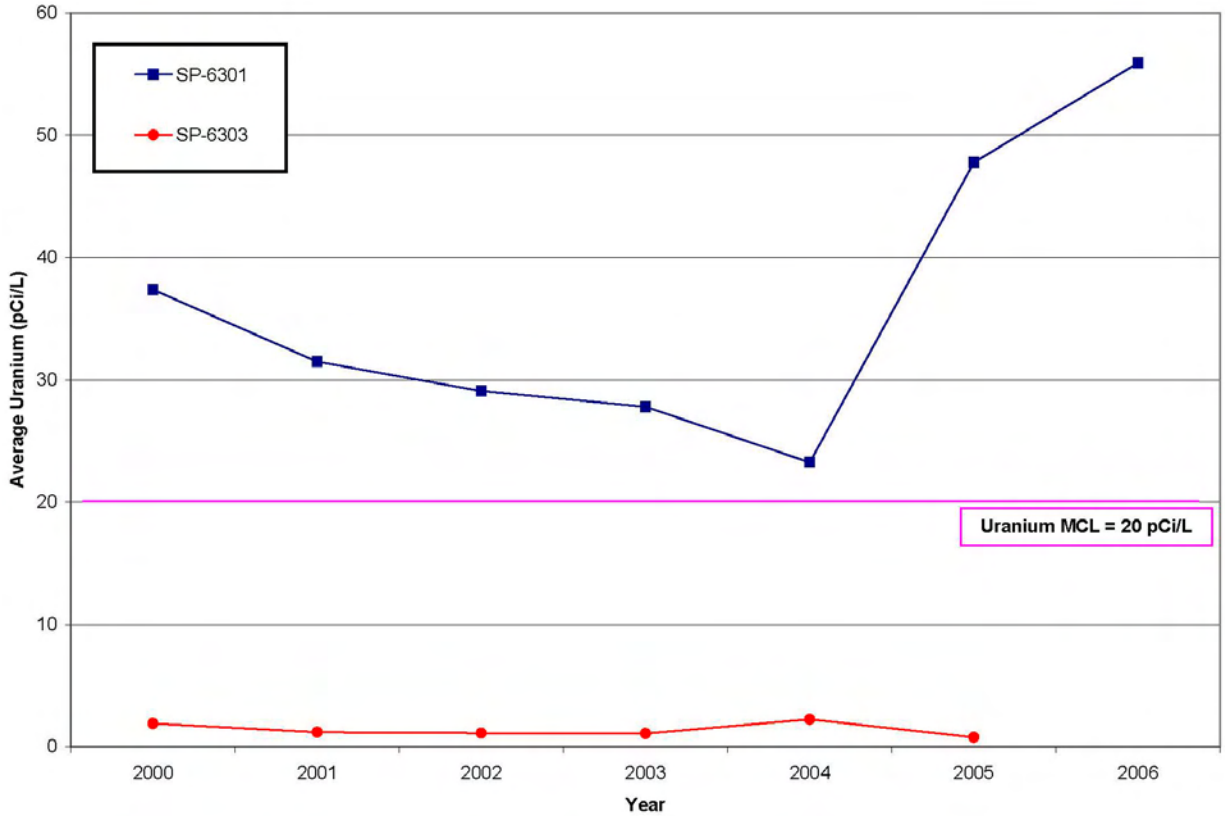

Figure 3–21. Annual Average Uranium Levels in Burgermeister Spring and SP-6303 (2000−2006)

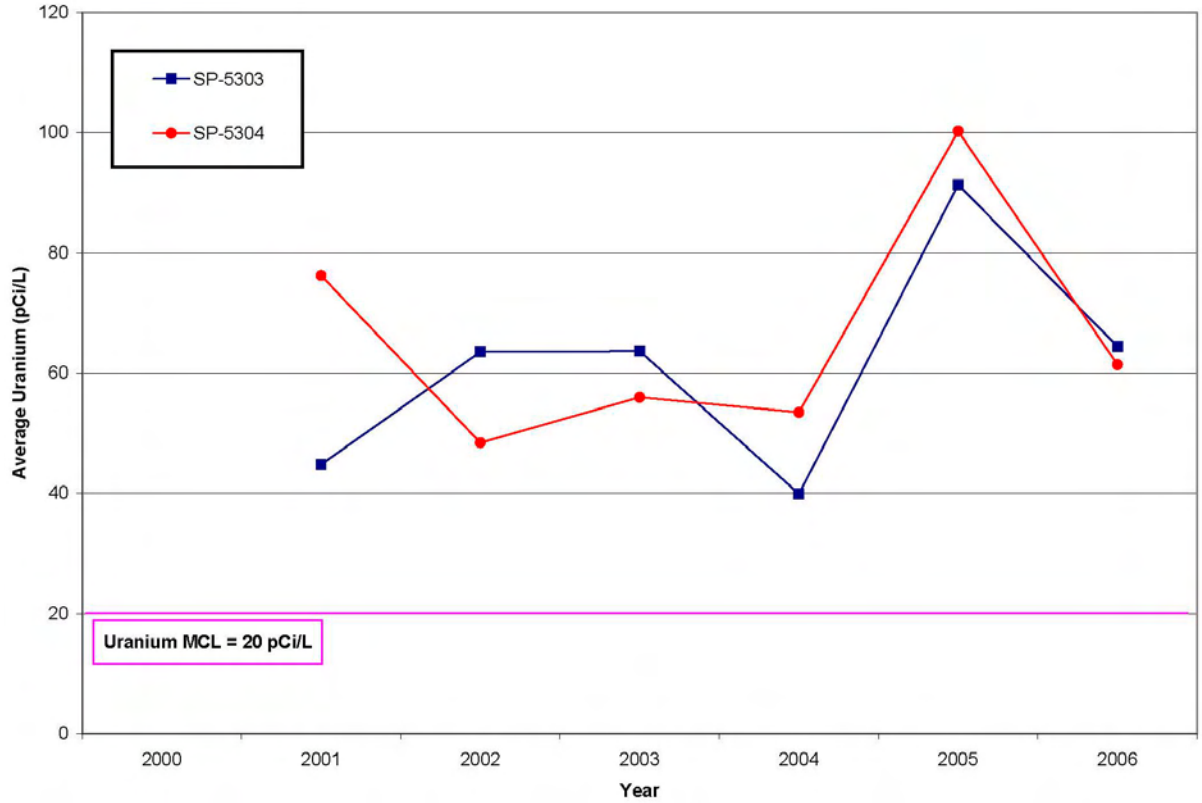

Figure 3–22. Annual Average Uranium Levels in Southeast Drainage Springs (2000−2006)

4.0 Reevaluation of Remediation Timeframes

Baseline monitoring was performed to acquire a comprehensive set of data to reevaluate the MNA remediation timeframes previously developed during the remedial design phase of the GWOU. It was anticipated that contaminant concentrations would be variable for some time due to the recent completion of source removal; the completion of several active groundwater field studies; and the reconfiguration of the site topography, which reduces the infiltration of runoff.

4.1 Recalculation of Initial Concentrations

As outlined in the RD/RA work plan (Appendix A, "Method for Reevaluating MNA Timeframes for GWOU Remedial Action Period" [DOE 2004b]), new baselines for MNA timeframes would be established for the COCs after the baselining period (at least 2 years). The average concentration for each COC for each well was calculated from the data collected during the baselining period (2004 through 2006). The re-estimation of the MNA timeframes was based on the average concentration from the averages of all the wells considered. Data was not available from all wells used during the 2002 timeframe estimation. A summary of the concentrations for each area is presented in Table 4–1.

Table 4–1. New Baseline Contaminant Concentrations for MNA Remediation Timeframe Determination

COC	Contour/Area	2002 Values		Baseline Period Values*
		Initial Concentration	Cleanup Time (years)	Initial Concentration
Nitrate (as N)	Contour 1/Area 1	198 mg/L	63	241 mg/L
	Contour 1/Area 2	173 mg/L	28	166 mg/L
Uranium	Contour 1	54 pCi/L	56	44 pCi/L
	Contour 2	29 pCi/L	4	62 pCi/L
TCE	Contour 1	61 µg/L	101	188 µg/L
2,4-DNT	Contour 1	0.43 µg/L	79	0.25 µg/L
	Contour 2	0.18 µg/L	9	0.10 µg/L
	Contour 3	114 µg/L	73	89 µg/L
2,6-DNT	Contour 5	66 µg/L	53	51 µg/L
2,4,6-TNT	Contour 2	75 µg/L	5	20 µg/L
1,3-DNB	Contour 1	1.7 µg/L	4	0.67 µg/L
Nitrobenzene	Contour 1	69 µg/L	9	< 0.09 µg/L

*Average of 2004–2006 data

Data from the two newer unweathered unit wells were not included in this reevaluation. It has been determined that additional data are likely needed to establish better baseline concentrations for nitrate and uranium at these two locations.

A comparison of the initial concentrations (C_0) used in 2002 and the new initial concentrations indicates that the values are relatively similar for most of the contaminants. Higher initial concentrations were calculated for nitrate (Contour 1/Area 1), uranium (Contour 2), and TCE (Contour 1).

4.2 Review of Areal Distribution of Contaminants

A review of the contaminant distributions in the shallow groundwater at the chemical plant from 2002 and the baseline period (2004 through 2006) shows that the areal distribution of the contaminants is essentially unchanged. Some elongation of the plumes may have occurred along the groundwater flow paths; however, changes in the distribution are minimal. Figures 3–1 through 3−8 depict the present distribution of contaminants in the shallow aquifer. Figures depicting the distribution of contaminants during 2002 are contained in Appendix A.

4.3 Review of MNA Remediation Timeframes

Because COC concentrations in areas of relatively high concentrations have tended to vary considerably in recent years, while very few trends in contaminant levels have been observed, the modeling performed in 2002 to evaluate MNA (ANL 2003a) is not revised in this report, and the projected cleanup times resulting from that earlier evaluation (Table 3–1) are considered applicable to the GWOU today. The projected time to clean up the GWOU remains at less than 100 years for all the contaminants, except TCE. The projected cleanup time for TCE increased from 100 years to approximately 145 years based on the revised baseline concentrations.

Although the initial concentrations for some areas have been calculated to be slightly greater than those used in 2002, the remediation timeframes for these contaminants were significantly less than 100 years, except for TCE. Also, the areal distributions of these contaminants have not changed significantly. In the case of TCE, the areal distribution has decreased somewhat, likely resulting in a remediation timeframe similar to the one calculated in 2002.

5.0 Monitored Network Assessment

The information presented in Section 3.0 regarding measured contaminant concentrations in groundwater and springs can be used to assess the appropriateness of the monitoring wells to fulfill their intended objectives and the sampling frequencies that have been established to track the progress of MNA in the GWOU. A summary of each objective is provided in the following sections. The revised monitoring program is presented in Table 6–1. The monitoring network is depicted in Figure 2–12.

5.1 Upgradient Wells (Objective 1)

The concentrations reported for the upgradient wells have been relatively stable. These wells have been sampled semiannually during the baseline period. The sampling frequency will be reduced to annual starting in calendar year 2008.

5.2 Performance Monitoring Wells (Objective 2)

The majority of the contaminant data trends in the Objective 2 wells have been stable during the baseline period, though variable data have been reported. Some increases in nitroaromatic compounds have been determined in the Frog Pond area; however, the cause of the changes has been identified and remedied. The sampling frequency for the Objective 2 wells has been semiannual. Due to variable data that are still reported for these locations, semiannual sampling should be retained for the Objective 2 well.

The two Objective 2 unweathered wells (MW-3040 and MW-4040) that were recently installed still display variable results. These wells will be kept on a quarterly frequency for at least 1 year (calendar year 2008) so a more comprehensive data set can be collected for evaluation.

5.3 Detection Monitoring Wells (Objectives 3 and 4)

Concentrations at downgradient (laterally and vertically) and fringe locations have been behaving as expected. These locations have been sampled at least semiannually during the baseline period. The sampling frequency will be reduced to annual starting in calendar year 2008.

A well (MW-4042) has been installed in the base of the Burlington-Keokuk Limestone as a candidate for an Objective 4 well in the former raffinate pit area. Samples will be collected on a quarterly basis for at last 2 years (starting in August 2007) to obtain a comprehensive data set to evaluate its adequacy as an Objective 4 well beneath the area of uranium and nitrate impact in the upper portion of the unweathered unit in this area.

5.4 Springs (Objective 5)

The majority of the contaminant data trends in the springs have been stable during the baseline period; however, variable data have been reported at Burgermeister Spring. Some increases in uranium have been determined for this spring. The sampling frequency for the springs has been semiannual. Due to variable data that are still reported for some of the springs and the variable data that have been reported for some of the Objective 2 wells, quarterly sampling will be performed for the Objective 5 springs starting in 2008.

Table 5–1. Monitoring Program for GWOU MNA Remedy

Location	Objective	Unit	Sampling Frequency	TCE	Nitrate (as N)	Uranium	1,3-DNB	2,4,6-TNT	2,4-DNT	2,6-DNT	NB
MW-2012	Objective 2	Weathered	S				✓	✓	✓	✓	✓
MW-2014	Objective 2	Weathered	S						✓	✓	
MW-2017	Objective 1	Weathered	A				✓	✓	✓	✓	✓
MW-2021	Objective 4	Unweathered	A		✓						
MW-2022	Objective 4	Unweathered	A		✓		✓	✓			
MW-2023	Objective 4	Unweathered	A				✓	✓	✓	✓	✓
MW-2032	Objective 3	Weathered	A				✓	✓	✓	✓	✓
MW-2035	Objective 1	Weathered	A	✓	✓	✓			✓		
MW-2038	Objective 2	Weathered	S		✓				✓		
MW-2040	Objective 2	Weathered	S		✓						
MW-2046	Objective 2	Weathered	S					✓			
MW-2050	Objective 2	Weathered	S						✓	✓	
MW-2051	Objective 3	Weathered	A				✓	✓	✓	✓	✓
MW-2052	Objective 2	Weathered	S						✓	✓	
MW-2053	Objective 2	Weathered	S					✓	✓	✓	
MW-2054	Objective 2	Weathered	S						✓	✓	
MW-2056	Objective 4	Unweathered	A				✓	✓	✓	✓	✓
MW-3003	Objective 2	Weathered	S		✓	✓					
MW-3006	Objective 4	Unweathered	A	✓	✓	✓			✓		
MW-3024	Objective 2	Weathered	S			✓					
MW-3030	Objective 2	Weathered	S	✓		✓			✓		
MW-3031	Objective 3	Weathered	A	✓		✓					
MW-3034	Objective 2	Weathered	S	✓	✓				✓		
MW-3037	Objective 3	Weathered	A	✓		✓			✓		
MW-3039	Objective 2	Weathered	S						✓		
MW-3040	Objective 2	Unweathered	Q		✓	✓					
MW-4007	Objective 4	Unweathered	A	✓	✓						
MW-4013	Objective 2	Weathered	S		✓						
	Objective 3		A						✓	✓	✓

Table 5−1 (continued).Monitoring Program for GWOU MNA Remedy

Location	Objective	Unit	Sampling Frequency	TCE	Nitrate (as N)	Uranium	1,3-DNB	2,4,6-TNT	2,4-DNT	2,6-DNT	NB
MW-4014	Objective 3	Weathered	A		✓		✓	✓	✓	✓	✓
MW-4015	Objective 3	Weathered	A						✓	✓	✓
MW-4022	Objective 1	Unweathered	A		✓	✓					
MW-4023	Objective 1	Weathered	A		✓	✓					
MW-4026	Objective 3	Alluvium/SED	A			✓					
MW-4029	Objective 2	Weathered	S	✓	✓						
MW-4031	Objective 2	Weathered	S		✓						
MW-4036	Objective 3	Weathered	A	✓	✓	✓			✓		
MW-4039	Objective 3	Weathered	A				✓	✓	✓	✓	✓
MW-4040	Objective 2	Unweathered	Q		✓	✓					
	Objective 4		A	✓					✓		
MW-4041	Objective 3	Weathered	A	✓	✓	✓	✓	✓	✓	✓	✓
MW-4042	Objective 4	Unweathered	Q		✓	✓					
MWS-1	Objective 3	Weathered	A	✓	✓	✓			✓		
MWS-4	Objective 3	Weathered	A	✓	✓	✓					
MWD-2	Objective 4	Unweathered	A		✓	✓					
SP-5303	Objective 5	Spring	Q			✓					
SP-5304	Objective 5	Spring	Q			✓					
SP-6301	Objective 5	Spring	Q	✓	✓	✓	✓	✓	✓	✓	✓
SP-6303	Objective 5	Spring	Q	✓	✓	✓	✓	✓	✓	✓	✓
SW-2007	Objective 5	Stream	A	✓	✓	✓	✓	✓	✓	✓	✓

Objective 1 – Upgradient Locations
Objective 2 – Contaminant Plume
Objective 3 – Downgradient and Lateral Locations
Objective 4 – Locations Beneath the Area of Impact
Objective 5 – Springs
SED – Southeast Drainage
A – Annual S – Semiannual Q – Quarterly

End of current text

6.0 MNA Data Evaluation Process

The monitoring network is designed to provide data to show that natural attenuation processes are acting as predicted or to trigger the implementation of contingencies when these processes are not acting as predicted (i.e., an unexpected expansion of the plume or a sustained increase in concentrations within the area of impact). The data analysis and interpretation will satisfy the following:

- Upgradient conditions (Objective 1) have remained unchanged.
- Performance monitoring (Objective 2) indicates that concentrations within the area of impact are decreasing as expected.
- Detection monitoring (Objectives 3, 4, and 5) indicates if unacceptable expansion of the plume is occurring.

A discussion of a more comprehensive long-term data evaluation is also presented. This review will consist of evaluating the data over a longer period of time.

6.1 Upgradient Monitoring Data Evaluation

Groundwater data from the upgradient locations will be compared with the previously collected data from each respective location. If a statistically significant increase (defined as a concentration that exceeds the mean plus three standard deviations for the previous eight data points) is measured, then an investigation of the data point's validity will be initiated. For those locations that are "nondetect," a statistically significant increase is considered to be the respective cleanup standard measured for two consecutive sampling periods.

6.2 Performance Monitoring Data Evaluation

Concentrations of COCs are expected to decrease to cleanup standards within a reasonable timeframe (i.e., 100 years). A long-term trend analysis will be performed to confirm downward trends in COCs over time. Performance will be gauged against these trends. Some locations are expected to show temporary upward trends due to ongoing dispersion, analytical variability, or other factors; however, concentrations are not expected to exceed historical maximums.

Concentration (annual averages)-versus-time graphs at each well would then serve as visual indicators of MNA progress. Given the variations in COC concentrations that have been observed in recent years at some monitoring locations, it is possible that multiple years may pass before clear indications of this local natural attenuation become obvious.

Though data from individual wells may not immediately provide conclusive evidence of natural attenuation, metrics based on average concentrations in specific contaminated areas would provide evidence of downward trends in contaminant mass. With this approach, the arithmetic weighted mean concentrations of a COC at all Objective 2 wells within a specific contaminated area and from a single sampling event could be graphed over time. As with individual wells, the respective measures of average concentrations would be expected to decrease as time passed.

The complex nature of groundwater flow and transport in the chemical plant area suggests that contaminant concentrations during the next few years will likely fluctuate in response to the

temporally and spatially variable processes upon which MNA depends. For these reasons, it will be important to identify potential causes of data variability rather than prematurely concluding that natural attenuation is progressing rapidly or not progressing at all. To that end, knowledge of the numerous fate and transport processes that affect contaminant levels at the site will be crucial.

Examples of phenomena that have, in the past, caused relatively large fluctuations in COC concentrations include the subsurface disturbances resulting from pilot testing of enhanced remediation methods. In addition, anomalously large decreases in the concentration of nitroaromatic compounds during recent years at well MW-2012 in the Frog Pond area appear to be related to local land subsidence rather than the product of natural attenuation induced by dilution and dispersion. Similarly, the appearance of chemically reducing conditions in a well located north of the disposal cell (DOE 2005b) a few years ago, which resulted from the biodegradation of dead organic matter in the well, was determined to be a transient and anomalous phenomenon. Such occurrences and other occasional stresses on the groundwater system, such as episodic recharges from large storms and the changes in aquifer chemical conditions that may result, should be anticipated.

6.3 Detection Monitoring Data Evaluation

Contaminants are expected to continue to disperse within known preferential flow paths associated with bedrock lows (paleochannels) in the upper Burlington-Keokuk Limestone and become more diluted over time. If a statistically significant increase (defined as a concentration that exceeds the mean plus three standard deviations for the previous eight data points) is measured, then an investigation of the data point's validity will be initiated. For those locations that are "nondetect," a statistically significant increase is considered to be the respective cleanup standard measured for two consecutive sampling periods.

Corresponding concentration (annual averages)-versus-time graphs at each well would then serve as visual indicators of MNA progress on a local scale. Given the variations in COC concentration that have been observed in recent years at some monitoring locations, it is possible that multiple years may pass before clear indications of this local natural attenuation become obvious.

6.4 Hydrologic Data Evaluation

Site hydrological conditions over time are being monitored using all the wells included in the MNA network (Objective 1 through 4 wells in addition to those well listed for Objective 6) in order to identify any changes in groundwater flow that might affect the protectiveness of the selected remedy. The static groundwater elevations of the monitoring network will be measured to establish that groundwater flow is not changing significantly and resulting in shifts in contaminant migration.

Groundwater elevations will be calculated and evaluated to verify that the groundwater flow directions and rates are sufficient to support the attenuation of the contaminants in the predicted timeframes. Also, groundwater flow direction will be evaluated against the IC boundary to verify that the restricted-use area is adequate.

6.5 Trigger Levels

Trigger levels were set for each contaminant in the performance and detection monitoring locations in the event that increases occur unexpectedly. There are two triggers for each COC. The first trigger is set at what would be a statistically significant increase in a contaminant concentration at a location. ("Statistically significant" has previously been defined as a concentration that exceeds the mean plus three standard deviations for the previous eight data points.) If this occurs, then an investigation of the data point's validity will be initiated.

The second trigger has been established as a fixed concentration that indicates unacceptable increases in contaminant concentrations either within the area of impact (Objective 2), outside the area of impact (Objectives 3 and 4), or at discharge points (Objective 5). The trigger levels are summarized in Table 6–1. The justification for the development of these triggers is summarized in the RD/RA work plan (DOE 2004b). Concentrations that exceed the second trigger level will invoke a more vigorous response.

Table 6–1. Trigger Levels for Performance and Detection Monitoring at the GWOU

Parameter	Objective 1[a]	Objective 2	Objective 3 (near)	Objective 3 (far)	Objective 4	Objective 5
Nitrate	Mean + 3sd	1,350 mg/L	30 mg/L	10 mg/L	20 mg/L	20 mg/L
Uranium	Mean + 3sd	100 pCi/L	50 pCi/L	20 pCi/L	40 pCi/L	150 pCi/L
TCE	Mean + 3sd	1,000 µg/L	15 µg/L	5 µg/L	10 µg/L	5 µg/L
2,4-DNT						
East Plume	Mean + 3sd	2,300 µg/L	1.1 µg/L	0.11 µg/L	0.22 µg/L	0.22 µg/L
West Plume	Mean + 3sd	5 µg/L	0.55 µg/L	0.11 µg/L	0.22 µg/L	0.22 µg/L
2,6-DNT	Mean + 3sd	2,000 µg/L	13 µg/L	1.3 µg/L	2.6 µg/L	1.3 µg/L
2,4,6-TNT	Mean + 3sd	500 µg/L	11.2 µg/L	2.8 µg/L	5.6 µg/L	2.8 µg/L
1,3-DNB	Mean + 3sd	20 µg/L	4 µg/L	1 µg/L	2 µg/L	1 µg/L
NB	Mean + 3sd	50 µg/L	34 µg/L	17 µg/L	17 µg/L	17 µg/L

[a]Mean + 3sd = mean of previous eight measured concentrations plus three standard deviations

6.6 Long-Term Data Evaluation

Every 5 years, the progress of the MNA remedy will be reviewed and documented. This review should be performed in conjunction with the CERCLA 5-Year Review for the Weldon Spring Site. This review should include trending analysis for the past 5 years of data.

As outlined in the RD/RA work plan (DOE 2004b), trend analysis will be performed on Objective 2 and 5 locations to confirm downward trends in contaminant concentrations over time. The baseline data for each Objective 2 well and Objective 5 spring was trended (Section 3.3) using a non-parametric Mann-Kendall test. Primarily, these data show stable or downward trends for a majority of the wells. Upward trends were identified in some wells for a few nitroaromatic compounds. Trend analysis indicated stable concentrations for uranium in all of the springs except for Burgermeister Spring, where an upward trend has been calculated; however, the uranium levels do not approach historical highs.

This review will also contain an assessment of the monitoring program, including locations and sampling frequency. In future years, the behavior of the contaminant concentrations will become more predictable. At that time, the monitoring frequency can be decreased. Also, as the natural attenuation progresses, some wells and springs will exhibit concentrations that fall below the cleanup level. As this happens, the continued monitoring of these wells will not be necessary. A justification for decreasing monitoring frequencies and deleting monitoring locations will be summarized in a report documenting the last 5 years of data.

7.0 Summary

This report presents the findings from an evaluation of MNA processes in groundwater, during recent years, at the chemical plant area within the DOE Weldon Spring Site in eastern Missouri. Baseline monitoring was performed to acquire a recent and comprehensive set of data to reevaluate the MNA remediation timeframes previously developed during the remedial-design phase of the GWOU. Contaminant concentrations were expected to vary for some time due to the recent completion of source removal, the completion of several active groundwater field studies, and the reconfiguration of site topography (which reduces the infiltration of runoff).

Also, the data were used to assess the present monitoring program and suggest changes in locations and sampling frequencies. Baseline monitoring began in July 2004 and has continued into the first half of 2006.

A comparison of the initial concentrations (C_0) used in 2002 and the new initial concentrations indicates that the values are relatively similar for most of the contaminants. A review of the contaminant distributions in the shallow groundwater at the chemical plant from 2002 and the baseline period (2004 through 2006) shows that the areal distribution of contaminants are essentially unchanged. The modeling performed in 2002 to evaluate MNA (DOE 2003) is not revised in this report, and the projected cleanup times resulting from that earlier evaluation (Table 2–1) are considered applicable to the GWOU today. The projected time to clean up the GWOU remains approximately 100 years.

The monitoring network is designed to provide data to show that natural attenuation processes are acting as predicted or to trigger the implementation of contingencies when these processes are not acting as predicted (i.e., an unexpected expansion of the plume or a sustained increase in concentrations within the area of impact). Methods to review and interpret data that will satisfy the following criteria have been presented:

- Upgradient conditions (Objective 1) have remained unchanged.
- Performance monitoring (Objective 2) indicates that concentrations within the area of impact are decreasing as expected.
- Detection monitoring (Objectives 3, 4, and 5) indicates if unacceptable expansion of the plume is occurring.

Every 5 years, the progress of the MNA remedy will be reviewed. This review should be performed in conjunction with the CERCLA 5-Year Review for the Weldon Spring Site. This review should include a trending analysis of the past 5 years of data. This review will contain a trend analysis performed on Objective 2 and 5 locations to confirm downward trends in contaminant concentrations over time. This review will also contain an assessment of the monitoring program, including locations and sampling frequency. A justification for decreasing monitoring frequencies and deleting monitoring locations will be summarized in a report documenting the last 5 years of data.

End of current text

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Appendix A

Contaminant Distributions—2002 Data

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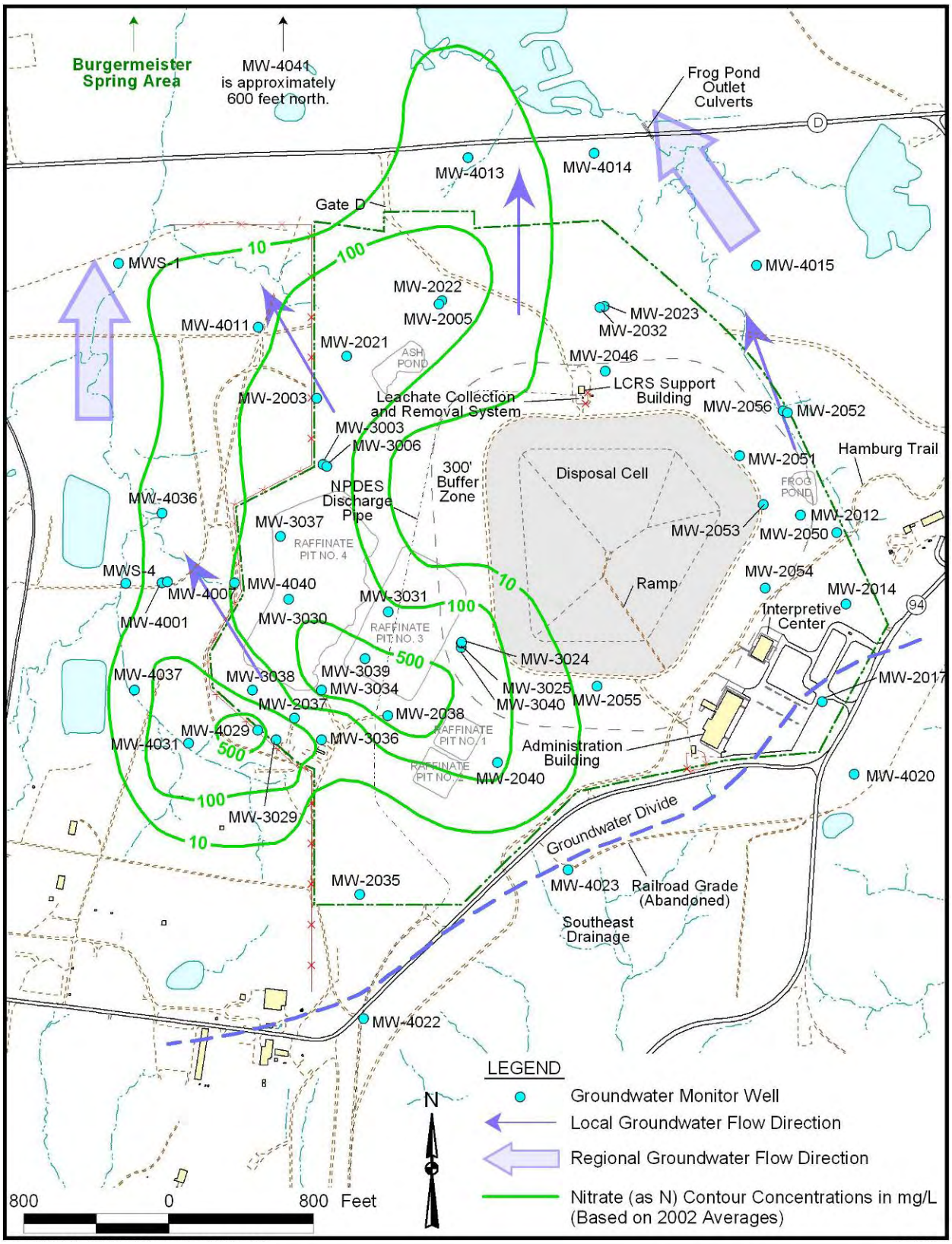

Figure A−1. Distribution of Nitrate in 2002 and Existing Monitoring Well Locations

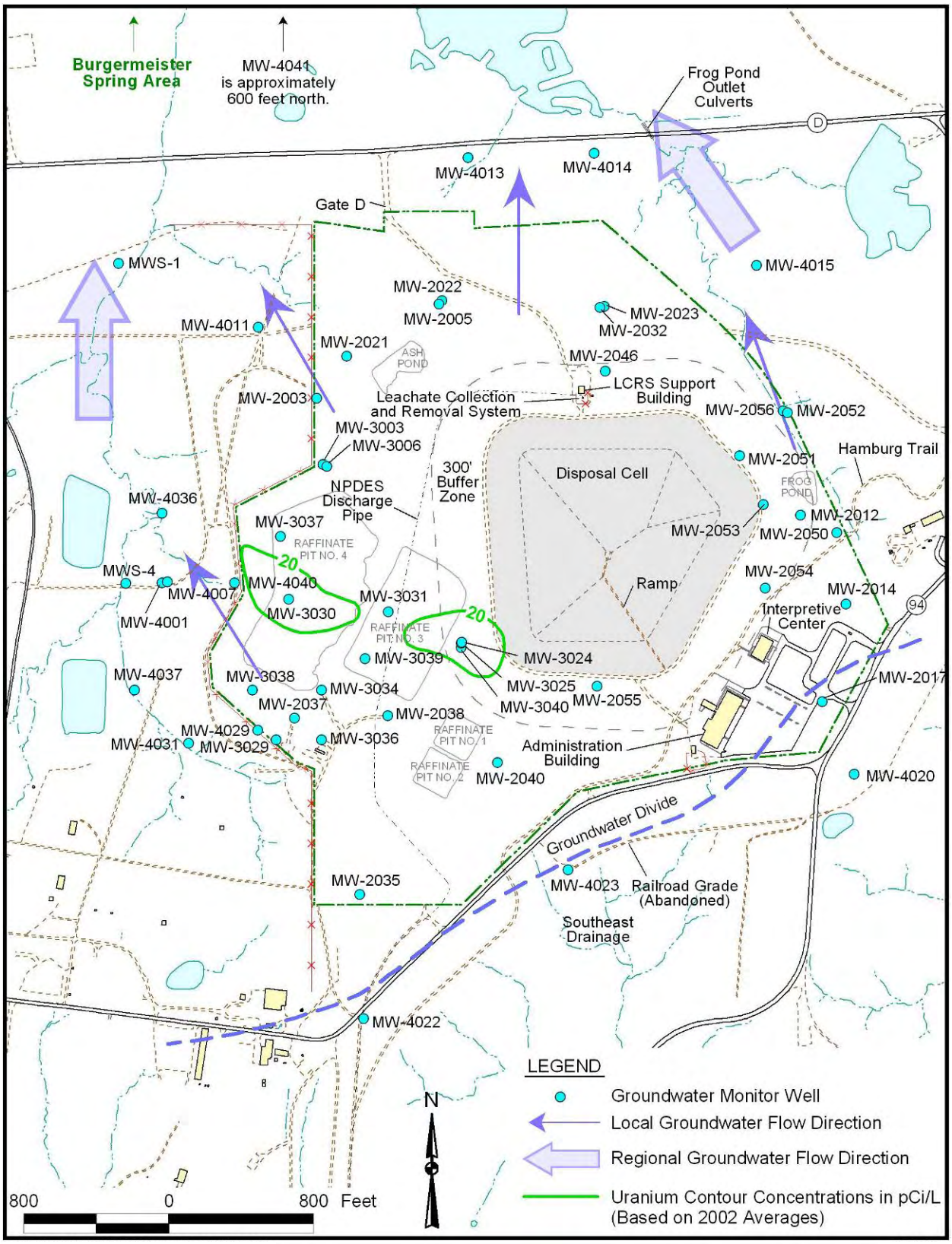

Figure A−2. Distribution of Uranium in 2002 and Existing Monitoring Well Locations

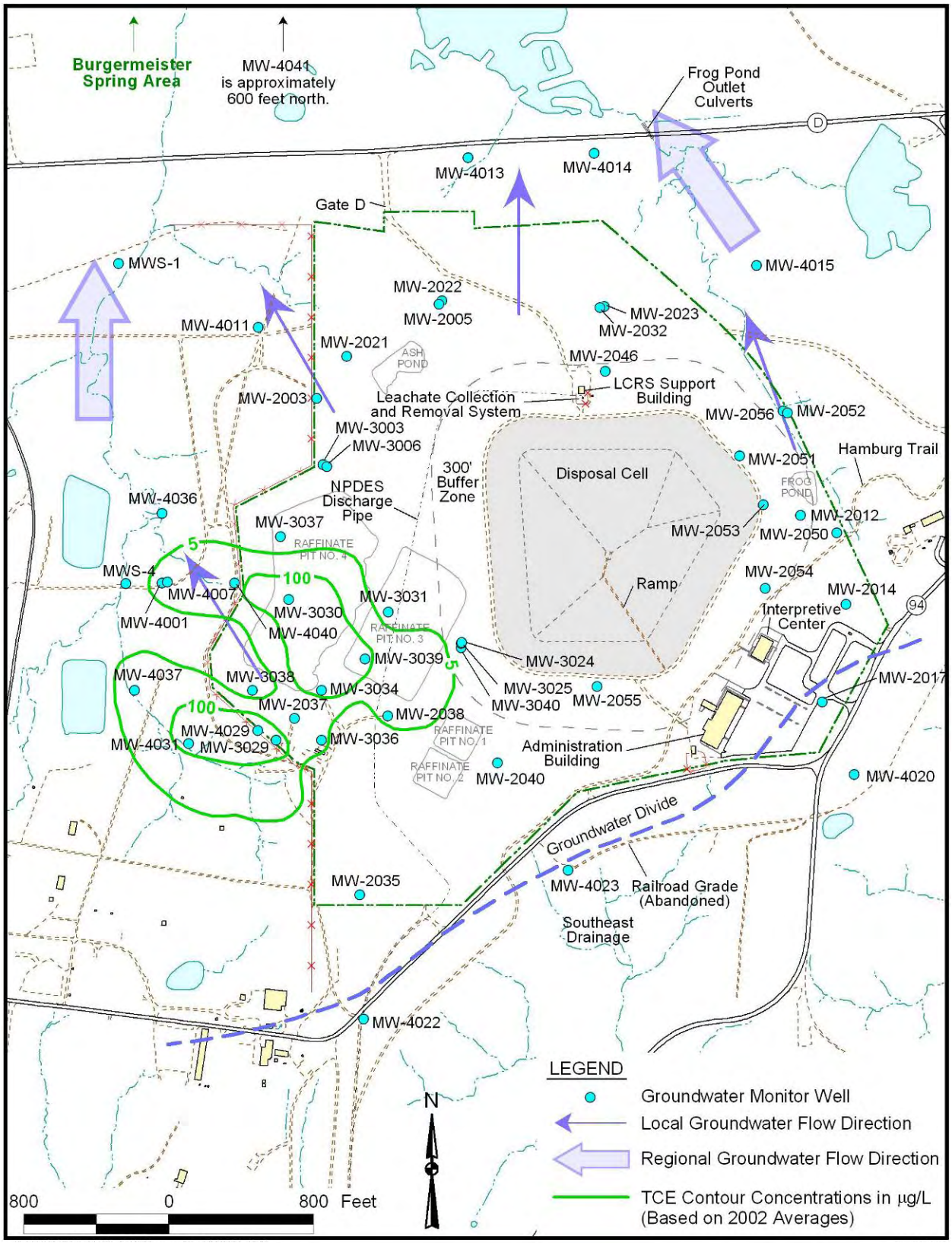

Figure A−3. Distribution of TCE in 2002 and Existing Monitoring Well Locations

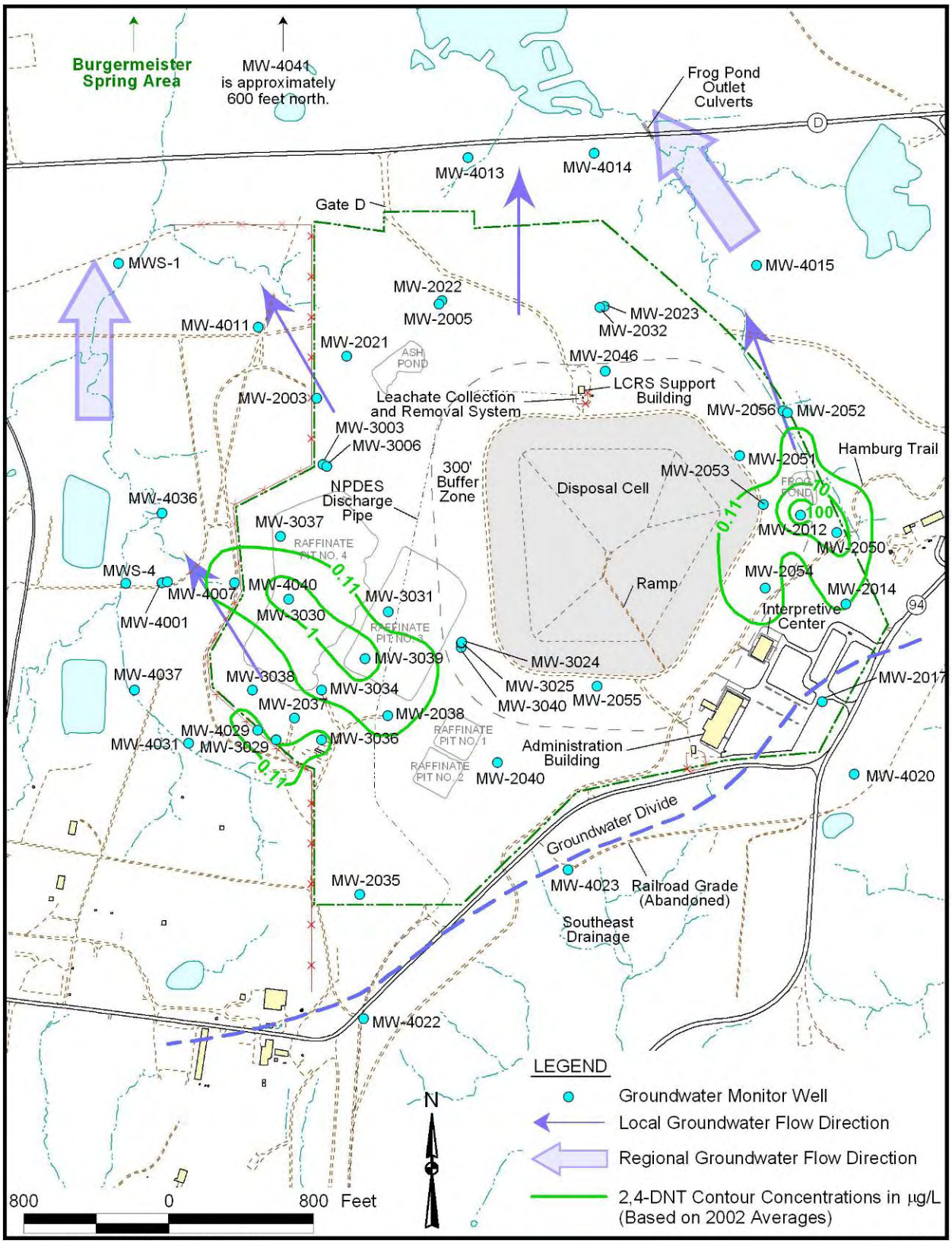

Figure A−4. Distribution of 2,4-DNT in 2002 and Existing Monitoring Well Locations

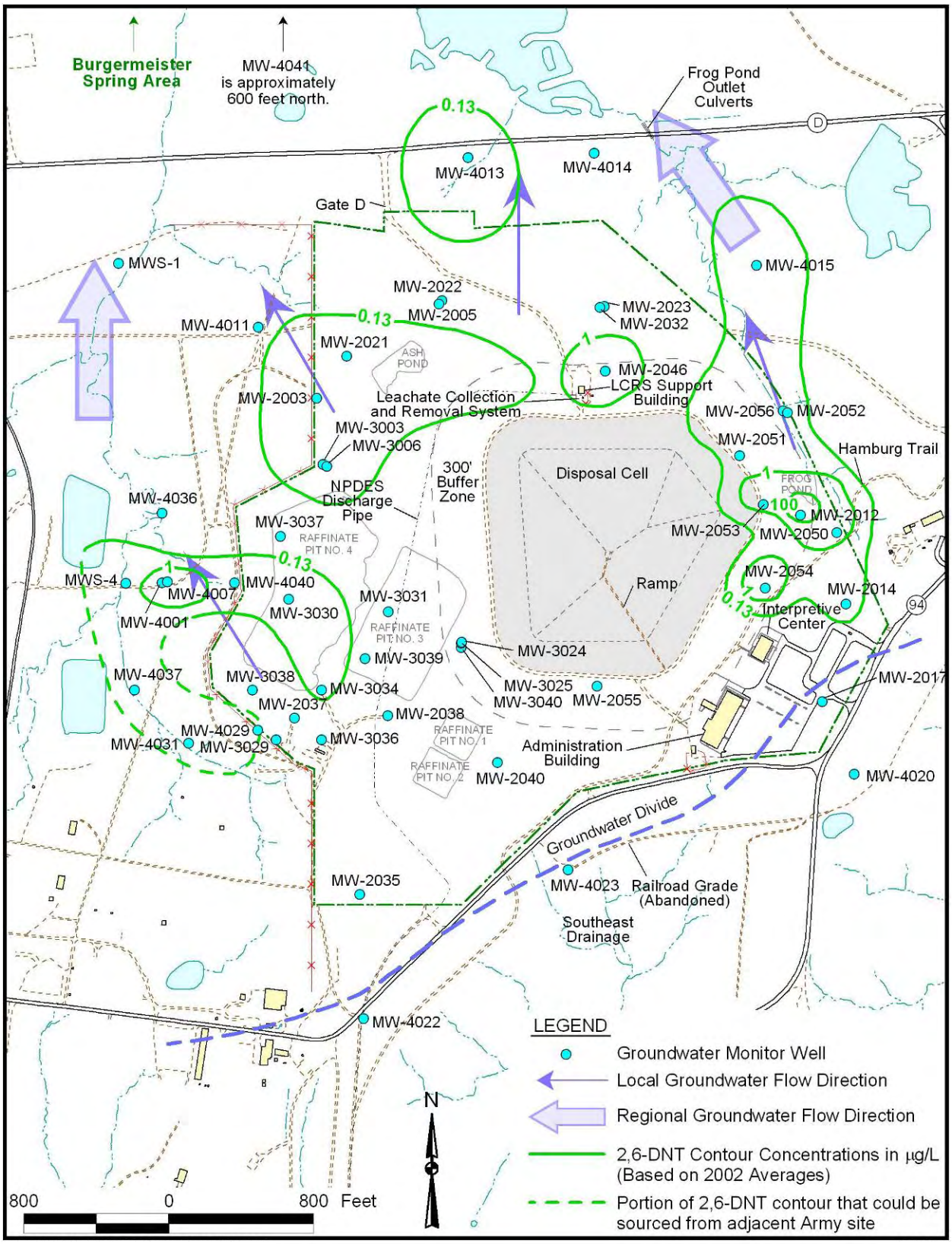

Figure A−5. Distribution of 2,6-DNT in 2002 and Existing Monitoring Well Locations

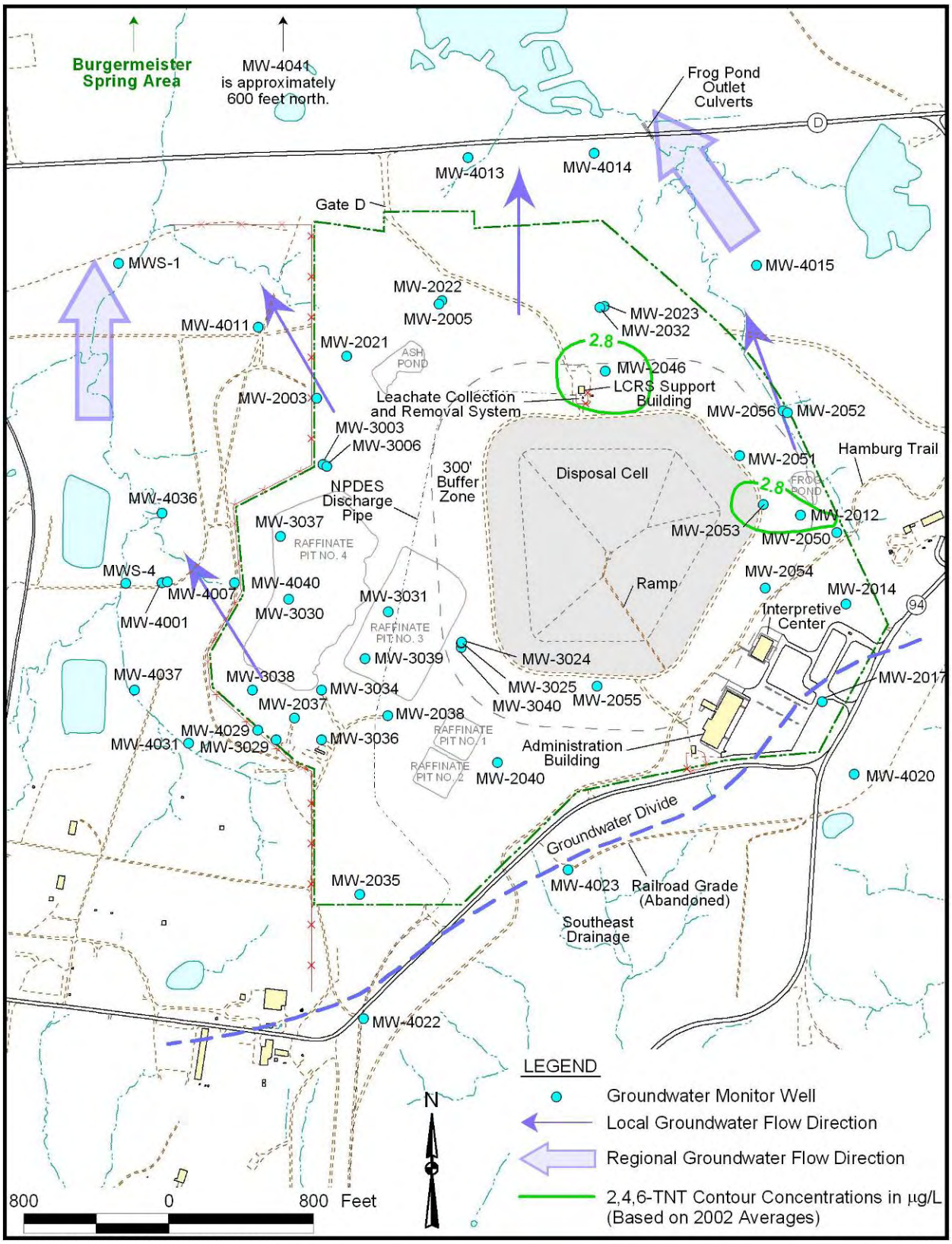

Figure A−6. Distribution of 2,4,6-TNT in 2002 and Existing Monitoring Well Locations