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Draft Supplemental Feasibility Study for Remedial Action for the Groundwater Operable Unit at the Chemical Plant Area of the Weldon Spring Site, Weldon Spring, Missouri

March 1999

U.S. Department of Energy
Weldon Spring Site Remedial Action Project
Weldon Spring, Missouri

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March 1999

prepared by

Environmental Assessment Division, Argonne National Laboratory

prepared for

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NOTATION

The following is a list of the acronyms, initialisms, and abbreviations (including units of measure) used in this document. Some acronyms used in tables or equations only are defined in the respective tables or equations.

ACRONYMS, INITIALISMS, AND ABBREVIATIONS

General

ACL	alternate concentration limit
ARAR	applicable or relevant and appropriate requirement
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
COC	contaminant of concern
DA	U.S. Department of Army
DNRA	dissimilatory nitrate reduction
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
FS	feasibility study (this document)
GAC	granular activated carbon
GWOU	groundwater operable unit
MCL	maximum contaminant level
MNA	monitored natural attenuation
NCP	National Oil and Hazardous Substances Contingency Plan
PRG	preliminary remediation goal
RA	remedial action
RD	remedial design
RI	remedial investigation
ROD	Record of Decision
SWTP	Site Water Treatment Plant
TBC	to-be-considered (requirement)

Chemicals

Cl^-	chloride ions
CO_2	carbon dioxide
1,2-DCE	1,2-dichloroethylene
1,3-DNB	1,3-dinitrobenzene
2-amino-4,6-DNT	2-amino-4,6-dinitrotoluene

Chemicals (Cont.)

4-amino-2,6-DNT	4-amino-2,6-dinitrotoluene
2,4-DNT	2,4-dinitrotoluene
2,6-DNT	2,6-dinitrotoluene
Fe^{2+}	ferrous ion
H_2O	water
Mn^{2+}	reduced manganese
Na^+	sodium ion
NO_3^-	nitrate
NO_2^-	nitrite
N_2O	nitrous oxide
N_2	nitrogen
NH_4^+	ammonium
O_2	ozone
TCE	trichloroethylene
1,3,5-TNB	1,3,5-trinitrobenzene
2,4,6-TNT	2,4,6-trinitrotoluene
UO_2	uranium dioxide
UO_2^{2+}	uranium dioxide ion
U(VI)	uranium in oxidized +6 valence state

UNITS OF MEASURE

cm	centimeter(s)	m	meter(s)
cm^3	cubic centimeter(s)	m^2	square meter(s)
ft	foot (feet)	µg	microgram(s)
ft^2	square foot (feet)	mg	milligram(s)
ft^3	cubic foot (feet)	mi	mile(s)
g	gram(s)	min	minute(s)
gal	gallon(s)	mV	millivolt(s)
gpm	gallon(s) per minute	pCi	picocurie(s)
in.	inch(es)	ppb	parts per billion
kg	kilogram(s)	ppm	parts per million
km	kilometer(s)	s	second(s)
L	liter(s)	yr	year(s)
lb	pound(s)		

DRAFT SUPPLEMENTAL FEASIBILITY STUDY FOR REMEDIAL ACTION FOR THE GROUNDWATER OPERABLE UNIT AT THE CHEMICAL PLANT AREA OF THE WELDON SPRING SITE WELDON SPRING, MISSOURI

1 BACKGROUND

This report is being prepared by the U.S. Department of Energy (DOE) as a supplement to the recently completed feasibility study (FS) report (DOE and DA 1998) for the groundwater operable unit (GWOU) at the Weldon Spring site. The GWOU addresses groundwater contamination at the chemical plant area. The Weldon Spring site is located in St. Charles County, approximately 48 km (30 mi) west of St. Louis (Figure 1).

1.1 CHEMICAL PLANT GWOU CONTAMINANTS OF CONCERN

Trichloroethylene (TCE), nitrate, nitroaromatic compounds, and uranium have been identified as the groundwater contaminants of concern (COCs). The primary sources of the contamination are the raffinate pits. Table 1 presents the maximum concentrations of the COCs for the 1997 to 1998 period. This list is inclusive of all wells that were reported to contain COC concentrations greater than the preliminary remediation goals (PRGs). The PRGs presented in Table 1 are based on applicable or relevant and appropriate requirements (ARARs), when available (as is the case for TCE, nitrate, 2,4-dinitrotoluene [2,4-DNT], nitrobenzene, and 1,3-dinitrobenzene [1,3-DNB]), or on risk-based values for the hypothetical resident scenario. The U.S. Environmental Protection Agency's (EPA's) proposed maximum contaminant level (MCL), which is considered a to-be-considered requirement (TBC), was used as a reference point in the evaluation presented in this supplement.

A number of the concentrations shown in Table 1 exceeded their associated PRGs or reference points. When plotted on a map of the chemical plant area, seven zones of contamination are indicated (Figure 2). Table 2 lists the COCs and maximum concentrations in each of the seven

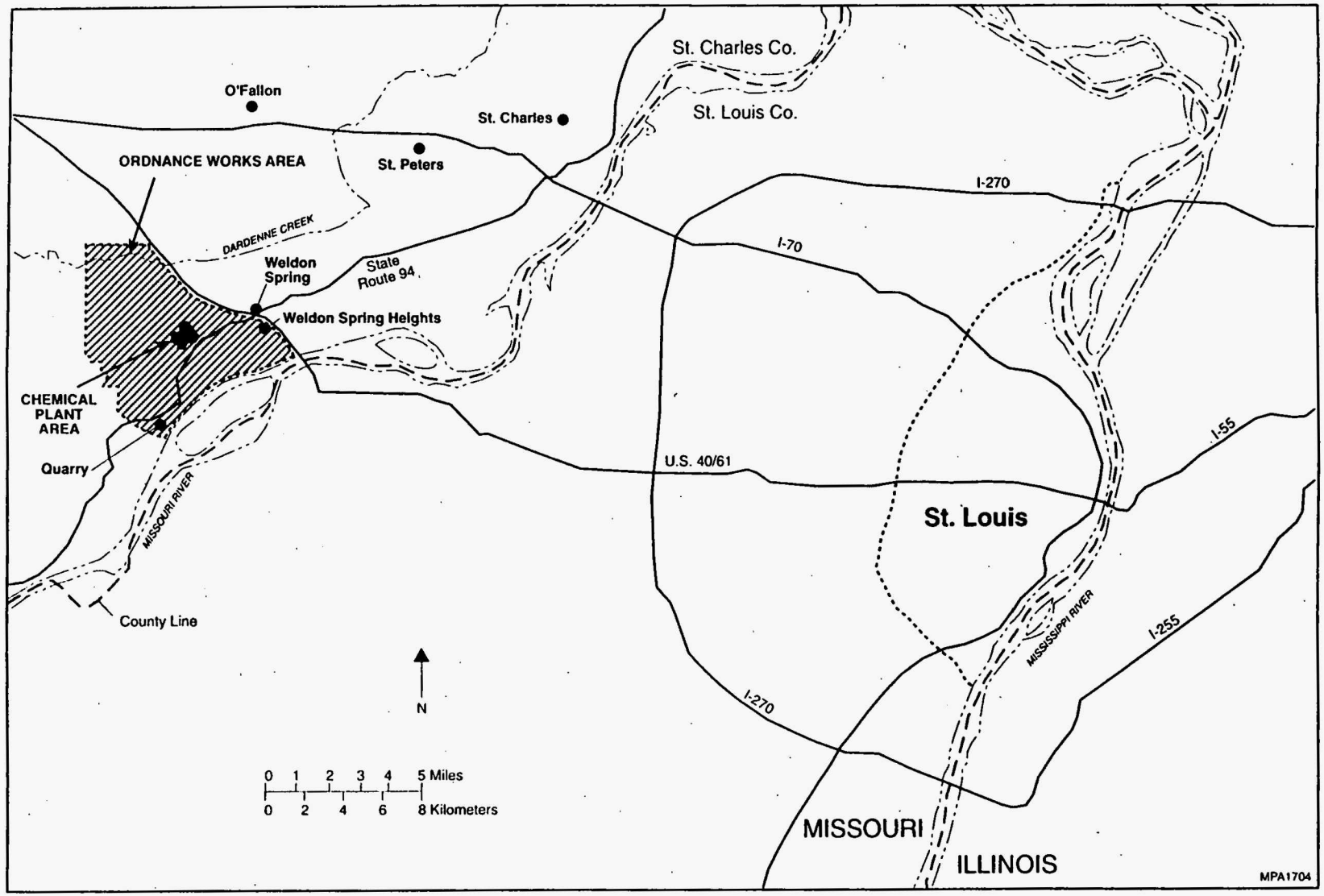

FIGURE 1 Locations of the Weldon Spring Chemical Plant and the Weldon Spring Ordnance Works

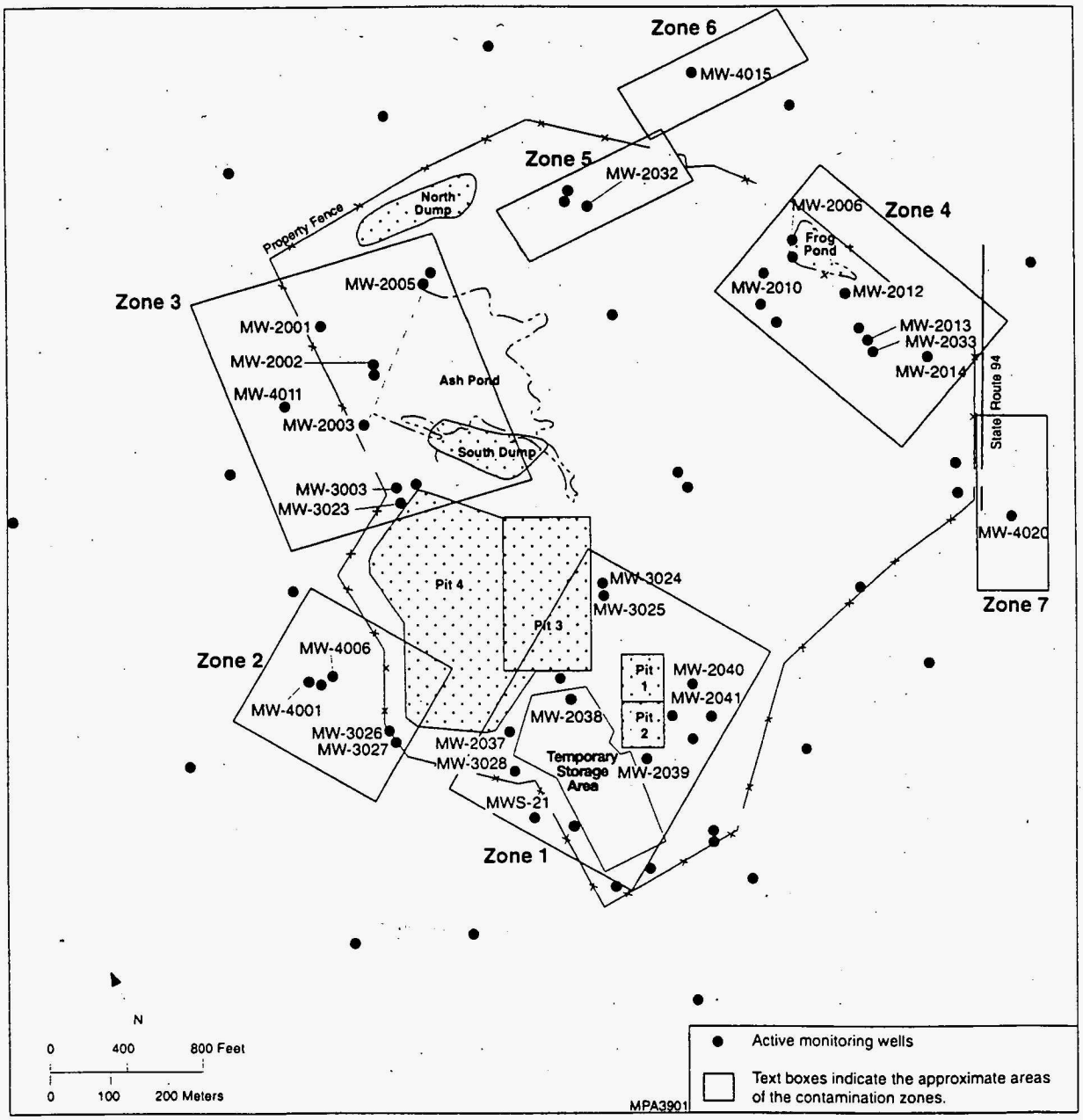

FIGURE 2 Contamination Zones at the Weldon Spring Chemical Plant Area

TABLE 1 Maximum Contaminant Concentrations for the GWOU Monitoring Network from 1997 to 1998[a]

Well	TCE (µg/L)	Nitrate (mg/L)	1,3,5-TNB (µg/L)	2,4,6-TNT (µg/L)	2,4-DNT (µg/L)	2,6-DNT (µg/L)	Uranium
PRG[b]	5	10	1.8	2.8	0.11	0.13	TBC (14 pCi/L)[c]
Weathered							
MW-2001	ND[d]	(80)	0.06	ND	0.08	0.06	7.5
MW-2002	ND	(90)	ND	ND	0.05	(0.26)	3.3
MW-2003	ND	(380)	ND	ND	(0.12)	(0.45)	6.0
MW-2005	ND	(160)	0.06	ND	0.05	0.11	6.8
MW-2006	ND	-[e]	(7.0)	ND	(0.13)	(1.3)	4.5
MW-2010	-	-	1.2	0.13	0.09	(0.66)	ND
MW-2012	ND	-	(7.2)	(25)	(6.0)	(110)	4.4
MW-2013	1.3	-	(4.3)	0.88	(0.17)	(2.1)	0.84
MW-2014	ND	-	(2.8)	ND	(0.16)	(0.50)	9.7
MW-2032	1.6	(110)	(2.0)	(4.4)	0.11	(1.3)	5.2
MW-2033	ND	-	(5.3)	1.4	(0.12)	(1.5)	6.2
MW-2037	(1,400)	(320)	0.20	ND	(0.73)	0.13	5.5
MW-2038	(1,200)	(1,000)	0.18	ND	(1.4)	(0.24)	4.0
MW-2039	ND	(88)	ND	ND	0.02	ND	6.1
MW-2040	ND	(170)	ND	ND	0.02	ND	4.6
MW-2041	ND	(210)	ND	ND	ND	ND	5.7
MW-3003	ND	(420)	ND	ND	(0.13)	(0.19)	(22)
MW-3023	0.03	(190)	ND	ND	(0.73)	(2.4)	(15)
MW-3025	(52)	(510)	ND	ND	0.10	(0.27)	3.6
MW-3027	ND	(450)	0.08	ND	0.04	0.04	3.2
MW-4001	(5.5)	(48)	(62)	2.4	(0.13)	(2.5)	2.4
MW-4006	ND	(23)	(21)	ND	0.10	(2.3)	3.9
MW-4015	ND	-	(7.1)	ND	0.08	(0.83)	3.2
MW-4020	ND	-	-	-	-	-	(20)
MWS-21	800	-	-	-	-	-	-
Unweathered							
MW-3024	ND	(460)	ND	ND	ND	ND	(55)
MW-3026	ND	(170)	0.07	ND	0.10	0.06	6.3
MW-4011	ND	(280)	ND	ND	0.01	0.06	8.4

[a] Concentrations are maximums reported for the COCs from data collected from 1997 through 1998. Concentrations in parentheses indicate that the respective PRG was exceeded.

[b] Preliminary remediation goals (PRGs) for trichloroethylene (TCE), nitrate, and 2,4-dinitrotoluene (2,4-DNT) are based on applicable or relevant and appropriate requirements (ARARs). For 1,3,5-trinitrobenzene (1,3,5-TNB), 2,4,6-trinitrotoluene (2,4,6-TNT), and 2,6-dinitrotoluene (2,6-DNT), the PRGs are risk-based concentrations for the hypothetical resident scenario.

[c] Although there is no ARAR for uranium in groundwater, for purposes of this analysis, the EPA's proposed MCL of 20 µg/L (equivalent to 14 pCi/L on the basis of the isotopic ratios of uranium in chemical plant groundwater), which is considered a TBC, was used as a reference point.

[d] ND denotes that the COC was not detected in the particular well.

[e] A hyphen indicates that the well was not sampled for that parameter.

TABLE 2 Contaminants of Concern for Zones at the Chemical Plant Area

Zone	Monitoring Wells with Contaminants Exceeding PRGs	Range of Maximum Contaminant Concentration						
		TCE (µg/L)	Uranium (pCi/L)	Nitrate (mg/L)	2,4-DNT (µg/L)	2,6-DNT (µg/L)	2,4,6-TNT (µg/L)	1,3,5-TNB (µg/L)
1	MW-2037, MW-2038 MW-2039, MW-2039 MW-2040, MW-2041 MW-3024, MW-3025 MWS-21	52–1,400	55	88–1,000	0.73–1.4	0.24–0.27	NA[a]	NA
2	MW-3026, MW-3027 MW-4001, MW-4006	5.5	NA	23–450	0.13	2.3–2.5	NA	21–62
3	MW-2001, MW-2002 MW-2003, MW-2005 MW-3003, MW-3023 MW-4011	NA	15–22	80–420	0.12–0.73	0.19–2.4	NA	NA
4	MW-2006, MW-2010 MW-2012, MW-2013 MW-2014, MW-2033	NA	NA	NA	0.12–6.0	0.50–110	25	2.8–7.2
5	MW-2032	NA	NA	110	NA	1.3	4.4	2.0
6	MW-4015	NA	NA	NA	NA	0.83	NA	7.1
7	MW-4020	NA	20	NA	NA	NA	NA	NA

[a] NA denotes that the particular COC was not detected, or that the reported concentration did not exceed the respective PRG or reference point.

contaminated zones and the monitoring wells associated with each zone. A range of maximum concentrations within each zone was provided in order to bracket calculations for cleanup times needed to meet the respective contaminant's PRG. In some cases, the range of contaminant concentrations found within a zone varied significantly (e.g., the TCE concentration in monitoring wells within Zone 1 varies from 52 to 1,400 ppb). Similarly, the nitrate concentration within Zone 1 ranges from 88 to 1,000 ppm. A single maximum concentration was used for zones that contained a single monitoring well (e.g., Zone 5; MW-2032).

1.2 CHEMICAL PLANT AREA HYDROGEOLOGY

The chemical plant area at the Weldon Spring, Missouri, site is situated above groundwater divides between the Missouri and Mississippi Rivers. The shallow groundwater aquifer beneath the chemical plant area is composed of fractured and weathered limestone. At the chemical plant, groundwater north of the divide flows to the north and discharges to springs and tributaries in the Mississippi River watershed, primarily Burgermeister Spring, a point of natural groundwater discharge near Lake 34 (DOE and DA 1997). Groundwater to the south of the divide flows to the south and southeast, primarily through the Southeast Drainage, and eventually discharges to the Missouri River. The presence of fractures, weathered features, and paleochannels in the top of the Burlington/Keokuk Limestone bedrock promote highly heterogeneous and complex flow patterns. The complexity of the shallow groundwater system is indicated by pronounced troughs in the potentiometric surface of the water table elevations. These troughs are associated with bedrock paleochannels and have been mapped through geologic borings and dye and tracer tests. The straight-line travel distance from the vicinity of the chemical plant area to Burgermeister Spring is approximately 1,981 m (6,500 ft); travel times have been measured at between two and three days, with velocities of up to about 0.6 m/min (2 ft/min).

In addition to the presence of conduits that transport groundwater rapidly from the chemical plant area to Burgermeister Spring, the composition of the shallow aquifer is also very heterogeneous. The water table occurs in materials that range from gravelly clay, clayey gravel, to limestone that is argillaceous, cherty, porous, vuggy, and fractured. Hydraulic conductivity (a hydrogeological parameter that indicates the ease with which an aquifer transmits water) varies from

about 1×10^{-5} to 1×10^{-2} cm/s. The weathered portion of the Burlington/Keokuk Limestone varies in thickness from about 3 to 15 m (10 to 50 ft).

Precipitation falling on the chemical plant area predominantly recharges the shallow groundwater aquifer, with little recharge to deeper groundwater systems (e.g., the St. Peters Sandstone). Groundwater movement is primarily horizontal because of the predominantly horizontal fracturing of the Burlington/Keokuk Limestone. The transport of dissolved contaminants occurs both in primary (porous medium) and secondary (fractures) porosity. Once the dissolved contaminants reach the conduit system, transport to points of discharge are very rapid and dilution by mixing can be substantial.

1.3 OBJECTIVE OF THE SUPPLEMENTAL FEASIBILITY STUDY

The information presented in this supplement will be used to augment the information presented in the FS (DOE and DA 1998) for the identification of the preferred alternative that will be presented in the Proposed Plan.

The nine preliminary alternatives developed and presented in the FS were:

- Alternative 1: No Action;
- Alternative 2: Long-Term Monitoring;
- Alternative 3: Natural Attenuation;
- Alternative 4: Groundwater Removal and On-Site Treatment Using Granular Activated Carbon (GAC) and Ion Exchange;
- Alternative 5: Groundwater Removal and On-Site Treatment Using Ultraviolet Oxidation (UV);
- Alternative 6: Groundwater Removal and On-Site Treatment Using Phytoremediation;
- Alternative 7: Removal and On-Site Treatment of Groundwater (in Zones 1 and 2);
- Alternative 8: In-Situ Treatment of TCE Using In-Well Vapor Stripping; and
- Alternative 9: In-Situ Chemical Oxidation of TCE Using Fenton-Like Reagents.

Of these alternatives, six (Alternatives 1, 2, 4, 7, 8, and 9) were retained for detailed evaluation in the FS.

Alternatives that involve groundwater extraction and treatment (Alternatives 4 and 7) are being evaluated further in this supplement in order to incorporate data obtained from a pump test conducted in the summer of 1998. This pump test indicated that the yield for groundwater extraction in the area of the pump test could be higher than the value assumed in the evaluation for the FS. However, dewatering of the aquifer occurred during the pump test. To avoid redundancy, only a discussion of Alternative 4 will be provided. Alternative 7 addresses an area discussed as Zones 1 and 2 under Alternative 4. In addition to TCE, nitrate, nitroaromatic compounds, and uranium are also present in Zones 1 and 2. The evaluation presented for Zones 1 and 2 in Chapter 3 for Alternative 4 addresses all the COCs.

Alternative 3: Natural Attenuation, which was screened out and not evaluated in detail for the FS, will be further evaluated in this supplement because more recent protocols have been made available since the initial screening of alternatives was conducted for the FS. Alternative 3 is referred to as "Monitored Natural Attenuation" in this supplement to be consistent with these protocols.

The detailed analysis presented in Chapters 2 and 3 evaluates Alternatives 3 and 4 relative to the threshold and balancing criteria stipulated in the National Oil and Hazardous Substances Contingency Plan (NCP) (EPA 1990). The two threshold criteria are as follows:

- Overall protection of human health and the environment, and
- Compliance with ARARs.

These threshold criteria ensure that the remedial action selected will be protective of human health and the environment, and that the action will attain ARARs identified at the time of the Record of Decision (ROD) or that it provides grounds for obtaining a waiver.

The balancing criteria are as follows:

- Long-term effectiveness and permanence;
- Reduction of toxicity, mobility, or volume through treatment;
- Short-term effectiveness;

- Implementability; and
- Cost.

The first two balancing criteria consider the preferences for treatment as a principal element and the bias against off-site land disposal of untreated waste. Cost-effectiveness is determined by evaluating three of the five balancing criteria: long-term effectiveness and permanence; reduction of toxicity, mobility, or volume through treatment; and short-term effectiveness. Overall effectiveness is then compared with costs to ensure that the costs are proportional to the overall effectiveness of a remedial action.

2 EVALUATION OF ALTERNATIVE 3: MONITORED NATURAL ATTENUATION

Monitored natural attenuation (MNA), as defined by the EPA, "refers to the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remedial objectives within a time frame that is reasonable compared to that offered by other more active methods" (EPA 1997). Natural attenuation processes include a variety of physical, chemical, and biological processes that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. Relevant physical processes include dilution, dispersion, and sorption; chemical processes include stabilization, destruction, and volatilization; and biological processes include stabilization or degradation by plants or microorganisms.

As with other remedies, cleanup at a contaminated site when using MNA is not complete until all cleanup objectives have been met. Monitoring is required to ensure that natural attenuation is occurring, to watch plume migration, and to identify any transformation products in order to protect potential receptors.

The evaluation presented in Section 2.1 discusses which natural processes could attenuate contaminant concentrations at the chemical plant area.

2.1 IDENTIFICATION OF NATURAL ATTENUATION PROCESSES FOR THE CHEMICAL PLANT GWOU

A detailed evaluation of each COC is presented in Sections 2.1.1 through 2.1.4. On the basis of these evaluations, it appears that the primary processes affecting all COCs in groundwater at the chemical plant are dilution and dispersion. Source removals being conducted per the chemical plant ROD (DOE 1993) are expected to prevent further groundwater contamination, and fresh rainwater and runoff that enter the aquifer over time will serve to dilute remaining groundwater contaminants. In some places, contaminant transport will occur slowly. In other areas, particularly those associated with the karst features, transport will be rapid with potentially large dilution.

On the basis of site geochemical conditions, biological degradation of TCE and the nitroaromatic compounds is unlikely to be occurring. Although DCE, which is an anaerobic degradation product of TCE, has been detected in a few wells, this DCE could be attributable to the original source of contamination. Low levels of DCE have been detected in a few wells where TCE has not been observed. Data from the site are not favorable for denitrification of nitrate or immobilization of uranium, both of which require reducing conditions. In addition to dilution and dispersion, uranium is also significantly attenuated by sorption in the overburden.

2.1.1 TCE

For the 1997 to 1998 sampling period, TCE has shown maximum concentrations of 1,300 and 950 µg/L in monitoring wells MW-2037 and MW-2038, which are located in the raffinate pit area. Lower concentrations were observed downgradient in wells MW-3025 (50 µg/L) and MW-4001 (5.5 µg/L) over the same time period. Natural processes that could affect TCE concentrations at a given site could include dilution, dispersion, sorption, and biodegradation.

2.1.1.1 Dilution and Dispersion

Fresh rainwater and runoff that enter the shallow aquifer over time will serve to dilute the TCE. Mechanical dispersion of the contaminant during transport will further decrease its concentration as its spatial extent increases.

2.1.1.2 Sorption

TCE has a low distribution coefficient (K_d) value in soil, approximately 0.074 to 0.24 mL/g (Montgomery 1996), which is expected to be even lower in the underlying bedrock. Because the K_d value is so small, sorption is not expected to play a role in attenuation of TCE at the GWOU.

2.1.1.3 Biodegradation

Biological processes are important for the degradation of organic compounds such as TCE in the environment. Plant activity can degrade TCE in the environment through rhizospheric degradation via microorganisms or phytoextraction of the TCE into the plant where it is broken

down by cell processes. In the case of volatile organic compounds (VOCs) such as TCE, some contaminants may be transpired to the atmosphere before complete degradation in the plant following phytoextraction (Chappell 1997). However, most of the contamination at the GWOU is located at depths greater than 5 m (16 ft) beyond the reach of plant activity.

Microorganisms can be categorized within three broad classes of degradation processes on the basis of the way in which the microorganisms use the contaminant (EPA 1998): (1) as the primary food source, (2) as an energy source (i.e., acts as an electron receptor), and (3) as a cometabolite. Microorganisms are capable of using organic contaminants as their primary food source under both aerobic and anaerobic conditions. TCE is not very susceptible to such degradation, however, because of its relatively high number of chlorine atoms per molecule.

In the case of microorganisms using a contaminant as an energy source, an anaerobic process, the reductive dechlorination of chlorinated hydrocarbons such as TCE appears to be the most important biological degradation process (EPA 1998). The chlorinated hydrocarbon is not used as the source of carbon, but rather acts as an electron acceptor to aid respiration of the microorganisms in these processes. For TCE, reductive dechlorination occurs by sequential dechlorination from TCE to 1,2-dichloroethylene (1,2-DCE) to vinyl chloride to ethene; other products may be produced, depending on the conditions within the aquifer. Table 3 lists the potential degradation products of TCE. The presence of 1,2-DCE, vinyl chloride, and ethene, and elevated concentrations of chloride are good indicators that TCE may be undergoing degradation (McCarty 1994; Wiedemeier et al. 1997).

Direct oxidation of vinyl chloride to carbon dioxide (CO_2) under Fe (III)-reducing conditions (i.e., mineralization to CO_2, water [H_2O], and chloride ions [Cl^-]) is one alternate decomposition pathway once the vinyl chloride degradation product has been formed (Bradley and Chapelle 1997). However, vinyl chloride, unlike its parent compound (TCE), can itself be used as a food source by microorganisms (EPA 1998). Vinyl chloride, which is an example of a contaminant that is more hazardous and mobile than its parent compound, has not been detected in chemical plant groundwater.

TABLE 3 Evaluation of Natural Attenuation for TCE in Chemical Plant Groundwater[a]

Process	Reaction or By-Product	Indicators	Site Data	Implication
Dilution	NA	Uncontaminated water entering the contaminated area.	The contaminated shallow aquifer is recharged by infiltrating rainwater and runoff.	The dilution of TCE in groundwater is occurring at the chemical plant.
Dispersion	NA	Increase in width of contaminated area in the direction of groundwater flow.	Width of contamination zone increased in direction of groundwater flow.	The dispersion of TCE in groundwater is occurring at the chemical plant.
Sorption	NA	TCE travels slower than average groundwater velocity.	• Site specific data would need to be collected. • TCE generally has a low K_d value in soils.	The sorption of TCE is not a significant natural process occurring in chemical plant groundwater.
Aerobic biodegradation	• Dichloroacetic acid • Glyoxylic • Formate • CO_2, H_2O, Cl^-	• Presence of degradation products. • Aerobic conditions.	• Data for the organic degradation products are not typically collected as part of a remedial investigation (RI). • Aerobic conditions exist in the shallow aquifer.	Site conditions may be favorable, but data would need to be collected to support a full determination.
Anaerobic biodegradation	• DCE • Vinyl chloride • Ethene • Ethane • CO_2, H_2O, Cl^-	• Degradation products. • $5 < pH < 9$. • < 0.5 mg/L O_2, not tolerated if $O_2 > 5$ mg/L. • < 1 mg/L nitrate. • TOC > 20 mg/L.	• DCE product is present. • pH range is favorable. • O_2, nitrate, and TOC levels are not favorable.	Site conditions are not favorable; DCE has been detected but could be part of the original contamination. Vinyl chloride has not been detected.

[a] Abbreviations: NA = not applicable; TOC = total organic carbon.

Conditions at the chemical plant site are not favorable for reductive dechlorination. Oxygen and nitrate levels must remain low, otherwise microorganisms will preferentially use oxygen first, then nitrate rather than TCE, as the electron acceptor. At the chemical plant site, dissolved oxygen concentrations have been measured to be greater than 1.0 mg/L in the shallow aquifer (DOE and DA 1997), and nitrate concentrations are greater than 1.0 mg/L in the raffinate pit area where the TCE contamination is located. However, dissolved oxygen concentrations greater than approximately 0.5 mg/L inhibit anaerobic bacteria, and nitrate levels greater than approximately 1.0 mg/L inhibit reductive dechlorination (EPA 1998). Therefore, site conditions do not appear to be conducive to reductive dechlorination.

Cometabolism results in biodegradation of an organic contaminant when it is not used as a food or energy source, but rather as the result of a secondary reaction. The secondary reaction may be catalyzed by enzymes produced during metabolism. A number of mono- and di-oxygenases have been observed to oxidize TCE through an epoxidation mechanism under aerobic conditions (Murray and Richardson 1993). Cleavage of the carbon-carbon double bond results in products such as dichloroacetic acid, glyoxylic acid, or formate and carbon monoxide (complete carbon-carbon bond cleavage), which are further broken down by heterotrophic organisms to CO_2 and H_2O.

It is unlikely that biodegradation of TCE is a significant natural attenuation process occurring at the chemical plant site, because the initial reductive dechlorination degradation product, DCE, has been detected only in monitoring wells MW-2037 and MW-2038 (MK-Ferguson 1997). This DCE could be indicative of the original contamination. Further degradation products such as vinyl chloride have not been detected (EPA 1998).

Further characterization not typically considered as data requirements in a remedial investigation (RI) would be necessary to determine the extent, if any, of TCE biodegradation. The characterization would include sampling for the ethene anaerobic degradation product and performance of a time series for chloride concentrations in wells with high TCE concentrations. Sampling would need to be conducted for the aerobic oxidation products such as dichloroacetic acid, glyoxylic acid, and formate. In addition, determination of the relative proportion of the cis- and trans-isomers of DCE would also need to be conducted as an indication of whether or not the DCE was

a degradation product. If the cis- isomer is greater than 80% of the DCE present, it is likely to be a degradation product (EPA 1998).

Another test (not typically considered as a data requirement for an RI) that could be conducted to determine whether TCE degradation is occurring is the use of chlorine isotope ratios. The relative abundance of the ^{35}Cl and ^{37}Cl isotopes in both the TCE and Cl ion can provide information as to whether or not some of the Cl^- ion in the groundwater was the product of TCE biodegradation (Sturchio et al. 1998). However, uncertainties in the evaluation of these data can arise if the TCE is not from the same source and exhibits a range of ^{35}Cl and ^{37}Cl isotope compositions, or the Cl^- ions in solution exhibit a range of isotope ratios.

Table 3 summarizes the evaluation for TCE; dilution and dispersion appear to be the primary processes for natural attenuation of TCE in chemical plant area groundwater.

2.1.2 Nitrate

Nitrate contamination is found in the shallow aquifer in the raffinate pit area and extends to the north toward the Ash Pond and North Dump areas. The highest nitrate concentration observed during sampling in 1997 to 1998 was 1,000 mg/L in monitoring well MW-2038, which is located south of raffinate pit 3. Natural attenuation processes applicable to nitrate at a given site could include dilution, dispersion, sorption, chemical stabilization, and biodegradation.

2.1.2.1 Dilution and Dispersion

Fresh rainwater and runoff that enter the shallow aquifer over time will serve to dilute the nitrate. Mechanical dispersion of the contaminant during transport will further decrease its concentration as its spatial extent increases.

2.1.2.2 Sorption

Nitrate is a highly soluble species that does not readily sorb to aquifer materials. Sorption experiments using soils from under the raffinate pits showed essentially no adsorption of nitrate under a range of pH conditions (Schumacher and Stollenwerk 1991). Thus, sorption is not a major attenuation mechanism for nitrate at the GWOU.

2.1.2.3 Chemical Stabilization

Inorganic ions such as nitrate can undergo abiotic chemical reactions (e.g., mineral formation) or complexation (e.g., precipitation reactions) with positively charged species or cations in an aquifer. However, chemical stabilization of nitrate is not significant because most inorganic nitrate compounds are readily soluble in water. The abiotic reduction of nitrate in the environment by reduced species such as reduced manganese (Mn^{2+}) or the ferrous ion (Fe^{2+}) in a groundwater aquifer is debatable. The chemical reactions are thermodynamically favorable, but past evidence suggests that bacteria are necessary (Korom 1992).

2.1.2.4 Biodegradation

Plant uptake of nitrate is a major attenuation process observed in nature and has been used as a site cleanup remedy in a number of cases where near-surface groundwater has been contaminated. As mentioned previously for the other contaminants, biodegradation by plants is possible, but much of the contamination at the site is found at depths beyond plant root systems (> 5 m [16 ft]). Therefore, biodegradation is not a viable natural attenuation process for this site.

Denitrification is the common term for the bacterial process involving the reduction of nitrate (NO_3^-). This biodegradation process involves several sequential steps; in the first, NO_3^- is reduced to nitrite (NO_2^-), which is further reduced to the gaseous nitric oxide (NO), followed by nitrous oxide (N_2O), and finally nitrogen (N_2). Some bacteria can only perform one or two steps, while others can mediate the entire process from NO_3^- to N_2 (Hiscock et al. 1991; Korom 1992). Thus, the presence of dissolved NO and N_2O intermediates at elevated concentrations, as well as elevated N_2 concentrations, indicates that denitrification is occurring.

A source of energy (electron donors) for the bacteria and anaerobic conditions is required for denitrification to occur. Heterotrophic bacteria use a carbon-based energy source. Groundwater cleanup at some organic contaminant sites (e.g., TCE) has included adding NO_3^-, in addition to an organic such as methanol as nutrients, for bacterial remediation of the more complex organic contaminant (EPA 1998). Autotrophic bacteria use an inorganic-based energy source such as Mn^{2+}, Fe^{2+}, or sulfides in solution; these bacteria obtain their carbon from CO_2 (Korom 1992). For the electron acceptor, bacteria will preferentially use oxygen because it yields the most energy to the

bacteria. Nitrate will then be used by facultative bacteria as the electron receptor if oxygen levels become insufficient. Oxygen levels must be lower than 0.2 mg/L for some bacteria to denitrify (Hiscock et al. 1991); others will denitrify in groundwater with up to approximately 5 mg/L of oxygen (Korom 1992). In addition to these factors, values of Eh below 350 mV are indicative of conditions favorable for denitrification (Keeney 1973; Hendry et al. 1983).

A competing reaction with denitrification under certain conditions is dissimilatory nitrate reduction (DNRA) to ammonium (NH_4^+). The generation of ammonium does not remove the nitrogen from the system as does denitrification. Consequently, future oxidizing conditions could regenerate the NO_3^- in the groundwater. Contributions from ammonium sorbed to clay materials have been postulated as a significant source of NO_3^- contamination as part of an annual cycle (Srinivasa 1998). Tiedje et al. (1982) have suggested that DNRA dominates when NO_3^- (electron acceptor) concentrations are limited, and denitrification dominates when carbon (electron donor) concentrations are limited. However, definitive evidence for this theory is lacking (Korom 1992).

Environmental conditions at the chemical plant GWOU may support denitrification of nitrate in some localized areas; overall, however, denitrification is not expected to be a significant process at the chemical plant. Values for pH are reasonable across the site; Eh potentials in the area north of the raffinate pits (i.e., wells MW-2001 to MW-2005 and MW-3003), however, are high, typically greater than 450 mV (Schumacher 1990). Denitrification is not expected in these areas. For the remaining monitoring wells, oxygen levels greater than 3 mg/L (not conducive to denitrification) have been observed.

Table 4 summarizes the results of the evaluation performed to determine which natural processes could be occurring in groundwater at the chemical plant area for attenuating nitrate concentrations. Dilution and dispersion appear to be the primary natural attenuation processes relative to nitrate.

2.1.3 Nitroaromatic Compounds

Low concentrations of nitroaromatic compounds have been observed in monitoring wells scattered across the chemical plant area. The compounds 2,4,6-trinitrotoluene (2,4,6-TNT), 2,4-dinitrotoluene (2,4-DNT), and 2,6-dinitrotoluene (2,6-DNT) were produced at the site. All three

TABLE 4 Evaluation of Natural Attenuation for Nitrate in Chemical Plant Groundwater

Process	Reaction or By-Product	Indicators	Site Data	Implication
Dilution	NA[a]	Uncontaminated water entering the contaminated area.	The contaminated shallow aquifer is recharged by infiltrating rainwater and runoff.	Dilution of nitrate is occurring at the GWOU.
Dispersion	NA	Increase in width of contaminated area in the direction of groundwater flow.	Broadening zone from source area.	Dispersion of nitrate is occurring at the GWOU.
Sorption	NA	Nitrate travels slower than average groundwater velocity.	• Soils from site showed no sorption. • Nitrate has a low K_d value in soils.	Sorption of nitrate is not a significant natural process occurring at the GWOU.
Chemical stabilization	Nitrate, unlike most anionic species, does not readily form insoluble compounds	• Decreasing nitrate groundwater concentration. • Increase of reaction products in groundwater or aquifer material.	Soils from site did not reduce the nitrate concentration in groundwater when saturated.	Chemical stabilization of nitrate is not a significant natural process occurring at the GWOU.
Biodegradation (denitrification)	• N_2 • NO • N_2O	• Favorable conditions – pH ≈ 7 to 9 – Eh ≈< 350 mV – O_2 ≈< 5 mg/L	Site conditions are not favorable, high Eh and O_2 levels.	Available data indicate that denitrification of nitrate is not a significant natural process occurring at the GWOU.

[a] NA = not applicable.

compounds are COCs, in addition to 1,3,5-trinitrobenzene (1,3,5-TNB), which is found in small concentrations in the 2,4,6-TNT product and production waste stream (DOE and DA 1998). Other nitroaromatic compounds identified in the GWOU include 1,3-DNB; nitrobenzene; 2-, 3-, and 4-nitrotoluene; 2-amino-4,6-dinitrotoluene (2-amino-4,6-DNT); and 4-amino-2,6-dinitrotoluene (4-amino-2,6-DNT). These latter compounds can be found in TNT manufacturing waste streams (Spanggord et al. 1982) and are also potential 2,4,6-TNT degradation products. Natural attenuation processes applicable to nitroaromatic compounds at a given site include dilution, dispersion, sorption, and biodegradation.

2.1.3.1 Dilution and Dispersion

Fresh rainwater and runoff that enter the shallow aquifer over time will serve to dilute the nitroaromatic compounds. Mechanical dispersion of the contaminants during transport will further decrease their concentrations as their spatial extent increases.

2.1.3.2 Sorption

Sorption tests of the primary nitroaromatic contaminants — 2,4-DNT, 2,6-DNT, and 2,4,6-TNT — indicated K_d values ranging from approximately 0.2 to 3.5 mL/g (DOE and DA 1997) in soils found in the Weldon Spring Training Area (WSTA). Lower values would be expected in the underlying bedrock. Thus, some attenuation from sorption is expected for nitroaromatic compounds. There is also some evidence for the irreversible binding of 2-amino-4,6-DNT and 4-amino-2,6-DNT to soils that would remove these species from solution (DOE and DA 1997).

2.1.3.3 Biodegradation

Biodegradation of nitroaromatic compounds could be an important natural process at a site. Degradation of nitroaromatic compounds by plants is possible (Schnoor 1997), but much of the contamination at the chemical plant site is found at depths (> 5 m [16 ft]) beyond plant root systems.

A number of investigators have examined the efficacy of microbial degradation as a mechanism for breaking up the nitroaromatic contaminants. Transformation of 2,4,6-TNT, 2,4-DNT, and 2,6-DNT can occur under both aerobic and anaerobic conditions (Preuss and Rieger 1995). Therefore, a wide variety of intermediate degradation products may be produced, depending on the degradation mechanism. However, the complete mechanism for degradation of the three primary nitroaromatic contaminants has not yet been established.

The initial degradation products of 2,4,6-TNT reduced by aerobic or anaerobic microorganisms are 2-amino-4,6-DNT and 4-amino-2,6-DNT. Further reduction of the remaining two nitro groups by aerobic microorganisms has not been observed (Preuss and Rieger 1995). Reduction of the remaining two nitro groups by anaerobic microorganisms (Stahl and Aust 1995) would result in triaminotoluene, which is unstable in the presence of oxygen because it is susceptible to autoxidation and polymerization (Preuss and Rieger 1995).

In the case of the GWOU, it has been shown that microorganisms indigenous to the soils and the affected aquifer have the ability to degrade TNT, 2,4-DNT, and 2,6-DNT. Laboratory tests using aquifer material have shown that mineralization of TNT, 2,4-DNT, and 2,6-DNT could occur (Bradley et al. 1994, 1997). The presence of 2-amino-4,6-DNT and 4-amino-2,6-DNT at the GWOU is indicative of 2,4,6-TNT degradation, but these compounds are also present in TNT production wastewater. Detection of further degradation products may also be inconclusive because at least 32 intermediate compounds have been identified in TNT production wastewater (Spanggord et al. 1982).

Table 5 summarizes the results of the evaluation performed to determine which processes might be naturally attenuating nitroaromatic compounds in chemical plant area groundwater. Dilution and dispersion appear to be the primary processes that attenuate nitrocromatic compounds in chemical plant groundwater.

2.1.4 Uranium

Uranium concentrations in four monitoring wells have been observed to exceed the proposed limit of 20 µg/L (14 pCi/L) during the 1997 to 1998 sampling period. Monitoring wells MW-3003 and MW-3023 (both of which are located near the northern edge of raffinate pit 4) and MW-4020 (located just outside the southeast site boundary) had maximum sample concentrations of 22, 15, and 20 pCi/L, respectively; these values are slightly greater than the proposed limit of 14 pCi/L. All three wells are completed in the weathered section of the shallow aquifer. A fourth well, MW-3024 (located on the east side of raffinate pit 3), had a higher maximum value of 55 pCi/L during this sampling period. The higher concentration in this well is believed to be the result of disturbances arising from cleanup operations in raffinate pit 3 during 1997. This well is completed in the unweathered section of the shallow aquifer, and, prior to 1997, the maximum uranium concentration in MW-3024 had been 4.2 pCi/L during the 1995 to 1996 sampling period. Natural

TABLE 5 Evaluation of Natural Attenuation for Nitroaromatic Compounds in Chemical Plant Groundwater

Process	Reaction or By-Product	Indicators	Site Data	Implication
Dilution	NA[a]	• Uncontaminated water entering the contaminated area. • Decreasing nitroaromatic groundwater concentration.	The contaminated shallow aquifer is recharged by infiltrating rainwater and runoff	Dilution of nitro-aromatic compounds is occurring at the GWOU.
Dispersion	NA	Increase in width of contaminated area in the direction of groundwater flow.	Width of contaminated zone increases in the direction of groundwater flow.	Dispersion of nitroaromatic compounds is occurring at the GWOU.
Sorption	NA	Nitroaromatic compounds travel slower than average groundwater velocity.	Site-specific data Kd values would need to be collected. However, nitroraromatics generally have a low K_d value in soils, estimated to range from approximately 0.15 to 1.3 mL/g.	Sorption of nitro-aromatic compounds may not be a significant natural process occurring at the GWOU.
Aerobic biodegradation	• Initial products during 2,4,6-TNT degradation are 2-amino-4,6-DNT and 4-amino-2,6-DNT.	• Oxidizing conditions in aquifer. • Reducing con-ditions in aquifer • Increase of reaction products in aquifer material.	• Oxidizing conditions in aquifer. • Initial degradation products of TNT are present (2-amino-4,6-DNT and 4-amino-2,6-DNT).	Some degradation products are present; however, these products are also part of the TNT manu-facturing waste stream.

TABLE 5 (Cont.)

Process	Reaction or By-Product	Indicators	Site Data	Implication
Anaerobic biodegradation	Initial products during 2,4,6-TNT degradation are 2-amino-4,6-DNT and 4-amino-2,6-DNT.	• Reducing conditions in aquifer • Increase of reaction products in aquifer material.	• Oxidizing conditions in aquifer • Initial degradation products of TNT are present (2-amino-4,6-DNT and 4-amino-2,6-DNT)	Evidence is inconclusive. Some degradation products are present; however, these products are also part of the TNT manufacturing waste stream, and conditions at the site are unfavorable for this degradation mechanism.

[a] NA = not applicable.

attenuation processes applicable at a given site to dissolved, radioactive metals such as uranium include dilution, dispersion, sorption, chemical or biological stabilization, and radioactive decay.

2.1.4.1 Dilution and Dispersion

Fresh rainwater and runoff that enter the shallow aquifer over time will serve to dilute the uranium. Mechanical dispersion of the contaminant during transport will further decrease its concentration as its spatial extent increases.

2.1.4.2 Sorption

A portion of many dissolved species is sorbed to solid materials within an aquifer. For uranium, some of the uranium will become sorbed on previously uncontaminated aquifer material as the contaminant plume migrates, thereby reducing the amount of uranium in solution. Sorption tests involving soil samples from the Ferrelview Formation and the clay till that underlies the raffinate pits suggest a range in K_d values from about 10 mL/g in the clay till to approximately 400 mL/g in the Ferrelview Formation (Schumacher and Stollenwerk 1991). Lower values are

expected in the bedrock formations where there are fewer sorption sites. Thus, the dissolved uranium is more likely to follow the groundwater flow than lag behind because of low sorption in the bedrock. Also, as more fresh water enters the aquifer, some sorbed uranium will desorb back into solution in an effort to maintain the K_d equilibrium value. Over time, both dissolved and sorbed contaminant concentrations will decrease as dilution and dispersion occur.

2.1.4.3 Chemical Stabilization

Uranium can also be removed from groundwater through chemical stabilization through the formation of an insoluble compound. The dominant soluble form of uranium found in the environment is the uranyl ion (UO_2^{2+}), in which uranium is in the oxidized +6 valence state, U(VI). The carbonate complex of the uranyl ion appears to be the primary uranium species in the groundwater at the chemical plant GWOU (DOE and DA 1997). However, U(VI) can be found in numerous insoluble minerals. One example, carnotite, was found within the raffinate pit sludges (DOE and DA 1997). Also, in the more reduced +4 valence state, uranium is relatively insoluble. Examples of these latter U(IV) compounds include uraninite (UO_2) and coffinite ($USiO_4$). Therefore, chemical reaction of the uranyl ion could form insoluble uranium compounds, thus removing uranium from the groundwater. These insoluble compounds are not available for sorption and desorption processes. Uranium would only be rereleased to the groundwater under conditions favoring reversal of the original reaction.

The reduction of uranium to insoluble U(IV) compounds was not observed in the raffinate pit sludges, and no uraninite has been observed in the chemical plant area (DOE and DA 1997). The formation of insoluble mineral phases is extremely hard to predict, although reducing conditions would provide evidence for the formation of insoluble U (IV) compounds. Groundwater Eh values in the contaminated area, however, are typically greater than 300 mV; dissolved oxygen concentrations are greater than 1 mg/L (Schumacher 1990), which is indicative of an oxidizing environment. Thus, chemical stabilization of uranium is not expected at the chemical plant GWOU.

2.1.4.4 Biological Stabilization

The accumulation of uranium in microorganism or plant biomass is another natural process that could lower contaminant groundwater concentrations. Some microorganisms are also known to reduce uranium to the insoluble U(IV) state during respiration (Barton et al. 1996). However, as discussed for TCE and nitrate, very little anaerobic biological activity is expected in the GWOU because of relatively high dissolved oxygen and Eh values. Thus, the precipitation of insoluble U(IV) species as a result of biological activity is not expected. If present, any aerobic activity that might accumulate uranium may periodically release some of the uranium as microbe populations grow and languish. The amount of organic carbon present in the aquifer is small (DOE and DA 1997); thus, the influence of any aerobic microbe populations present in the aquifer would be small when compared with sorption. The depth of contamination (> 5 m [16 ft]) also rules out the possibility of accumulation by plants.

2.1.4.5 Radioactive Decay

The primary uranium isotopes found at the site — uranium-234, -235, and -238 (> 99%) — have half-lives of 245,000, 8 million, and 4.5 billion years, respectively. Thus, radioactive decay is not a significant attenuation pathway for uranium at the GWOU.

Table 6 summarizes the results of the evaluation performed to determine the effects of natural processes on uranium in chemical plant area groundwater. The evaluation indicates that dilution and dispersion are the primary processes attenuating uranium concentrations in chemical plant groundwater.

2.2 TIME REQUIREMENTS TO ATTAIN PRGS FOR MONITORED NATURAL ATTENUATION

The evaluations presented in Section 2.1 indicate that for all COCs, dilution and dispersion are the primary natural attenuation processes. Therefore, this section provides calculations for estimating cleanup times to attain PRGs via these processes. Under the processes of dilution and dispersion, dissolved contaminants in the groundwater beneath the chemical plant area would move in the direction of natural groundwater flow. In general, this flow would be to the west and northwest

TABLE 6 Evaluation of Natural Attenuation for Uranium in Chemical Plant Groundwater

Process	Reaction or By-Product	Indicators	Site Data	Implication
Dilution	NA[a]	• Uncontaminated water entering the contaminated area. • Decreasing uranium groundwater concentration.	The contaminated shallow aquifer is recharged by infiltrating rainwater and runoff.	Dilution of uranium is occurring at the GWOU.
Dispersion	NA	Increase in width of contaminated area in the direction of groundwater flow.	Width of contaminated zone increases in the direction of groundwater flow.	Dispersion of uranium is occurring at the GWOU.
Sorption	NA	Uranium travels slower than average groundwater velocity.	Soils from the site were determined to have K_d ratios ranging from approximately 10 to 400 mL/g.	Sorption of uranium could be a significant natural process occurring at the GWOU.
Chemical stabilization	• Minerals • U(IV) compounds	• Reducing conditions in aquifer. • Increase of reaction products in aquifer material.	• Oxidizing conditions in aquifer. • U mineral formation was only noted in raffinate pit sludge. • No U(IV) compounds have been detected.	Chemical stabilization of uranium is not a significant natural process occurring at the GWOU.
Biological stabilization	U(IV) compounds	• Reducing conditions in aquifer. • Increase of reaction products in aquifer material.	• Oxidizing conditions in aquifer. • No U(IV) compounds have been detected.	Available data indicate that biological stabilization of uranium is not a significant natural process occurring at the GWOU.

[a] NA = not applicable.

for Zones 1 through 6, which are north of the groundwater divide. Groundwater flow in Zone 7 (MW-4020) would be toward the south and east because it is located south of the groundwater divide. The total flux (volume of contaminated water/time) of contaminated water out of a zone can be defined as

$$Flux = \frac{V_d}{\phi} A_t \phi = K \nabla h t W , \tag{2.1}$$

where

A_t = total area of the aquifer perpendicular to the direction of groundwater flow,

K = hydraulic conductivity of the porous medium material,

t = thickness of the aquifer,

V_d = Darcy's groundwater velocity,

W = width of the contaminated zone,

ϕ = effective porosity of the porous medium, and

∇h = hydraulic gradient present.

Darcy's velocity (Freeze and Cherry 1979) is given by

$$V_d = K \nabla h . \tag{2.2}$$

Ignoring any degradation processes, the number of pore volumes of contaminated water that must be discharged from a contaminated zone in order to meet cleanup criteria was defined as (Cohen et al. 1997) follows:

$$Number\ of\ pore\ volumes = R \ln(\frac{C_0}{C_w}) , \tag{2.3}$$

where R is the retardation coefficient for the contaminant of concern given by

$$R = 1 + \frac{\rho_b K_d}{\phi} , \tag{2.4}$$

and K_d is the contaminant's distribution coefficient (mL/g), ρ_b is the bulk density of the porous medium, ϕ is its effective porosity, C_0 is the initial contaminant concentration, and C_w is the contaminant's PRG.

A single pore volume for a contaminated zone was calculated by assuming that the contaminated zone was a parallelepiped, that is,

$$Pore\ volume = tLw\phi, \tag{2.5}$$

where L is the length of the contaminated zone in a direction parallel to the direction of groundwater flow.

The time required to reach the PRG by natural attenuation is obtained by integrating the volumetric flux over time. For a flux that is constant in time, the result is given by the following relationship:

$$\Delta t = \frac{R\ln(\frac{C_0}{C_w})twL\phi}{K\nabla htw} = \frac{Rln(\frac{C_0}{C_w})L\phi}{K\nabla h}. \tag{2.6}$$

Use of Equation 2.6 implies that once contaminated groundwater leaves a contaminated zone, it is removed from the system (i.e., downgradient locations that are initially clean do not become contaminated because of contaminant transport). For the chemical plant area, this assumption is reasonable for Zones 1 through 6 because of the proximity of paleochannels that transport contaminated groundwater rapidly to the vicinity of Burgermeister Spring where, historically, measured contaminant concentrations have been low because of dilution. Cleanup times for Zone 7 may be underestimated because of a longer travel path for contaminated water to move from the vicinity of well MW-4020 to the Southeast Drainage.

Dissolved contaminants in groundwater leaving the contaminated zones will be diluted by mixing with recharge water, mixing with water in the conduit system to either Burgermeister Spring or the Southeast Drainage, dilution with water in Lake 34, and dilution with water flowing in Dardenne Creek.

Initial dilution of the shallow groundwater occurs by mixing with infiltrating precipitation. A dilution factor for the process can be calculated with the following expression (Tomasko 1992):

$$Dilution\ factor = 1 + \frac{IL\phi}{K\nabla ht}, \tag{2.7}$$

where I is the effective recharge to the aquifer. Table 7 lists the dilution factors for the seven contaminated zones at the chemical plant area. These values were calculated with an average effective porosity of 0.28 and a gradient of 0.01. The maximum dilution occurs in Zone 3 (8.99). The least dilution occurs in Zone 5 (1.01) because of its very large hydraulic conductivity.

Additional dilution occurs when contaminated water from the chemical plant area mixes with initially clean water in the conduit system to either Burgermeister Spring or the Southeast Drainage. As discussed in the RI for the GWOU (DOE and DA 1997), about 80% of the effective recharge to the shallow groundwater system beneath the chemical plant area discharges in the vicinity of Burgermeister Spring. For an effective recharge of 6.4 cm/yr (2.5 in./yr) (Kleeschulte and Imes 1994), approximately 40 acre-feet of water per year would be discharged from the chemical plant area north of the groundwater divide. In calendar year 1996, the total flow from Burgermeister Spring was about 168 acre-feet (Kleeschulte 1997). For this flow, the discharge from the chemical plant area would be diluted by about a factor of 4 if all of the water from the chemical plant area discharged at Spring 6301. The total dilution of dissolved contaminants discharged from the seven zones of contamination would, therefore, range from about 4 to 36. Dilution for the Southeast Drainage is expected to be large because of an overland flow component from the surrounding terrain.

Table 8 shows the average concentrations in Burgermeister Spring (6301) and Spring 6303 for the COCs for 1997 and 1998 and their standard deviations. A comparison of these data with the maximum concentrations found in the first six zones of contamination indicates that dilution is occurring (groundwater flows to the Southeast Drainage from Zone 7). Dilution for nitrate ranges from about 3 to 140; dilution for 2,4-DNT ranges from about 2 to 28; dilution for 2,6-DNT ranges

TABLE 7 Average Concentrations and Standard Deviations for the Chemical Plant Area COCs at Burgermeister Spring (6301) and Spring 6303

Contaminant	1997 Average Value	1998 Average Value
Burgermeister Spring (6301)		
Uranium (pCi/L)	46 ± 36	62 ± 42
Nitrate (mg/L)	7.4 ± 8.1	2.8 ± 1.0
TNT (µg/L)	0.098 ± 0.03	0.072 ± 0.04
2,4-DNT (µg/L)	0.05 ± 0.04	0.05 ± 0.03
2,6-DNT (µg/L)	0.14 ± 0.004	0.19 ± 0.18
TNB (µg/L)	ND[a]	ND
TCE (µg/L)	ND	ND
Spring 6303		
TCE (µg/L)	1.5 ± 0.5	0.6 ± 0.3

[a] ND = not detected.

TABLE 8 Parameters Used for Contamination Zone Calculations

Zone	Width (ft)	Length (ft)	Thick (ft)	Volume (million ft^3)	Dilution	Average Hydraulic Conductivity (ft/yr)
1	1,520	1,120	33.1	15.8	1.06	3,414
2	1,000	800	20.6	4.6	1.46	497
3	1,700	1,400	28.4	19	8.99	36
4	1,200	1,200	18.6	7.5	1.28	1,345
5	1,000	500	10.3	1.4	1.01	41,380
6	1,000	500	20.5	2.9	5.74	30
7	1,000	500	16.2	2.3	8.50	24

from about 2 to 800; and dilution for TNT ranges from 45 to 250. The dilution for uranium is about 1.2. The uranium dilution may be anomalous because uranium may have been introduced into the conduit system by overland flow rather than a groundwater path and increases in concentration at Burgermeister Spring with increasing flow. Given the variability in the measured parameters at Burgermeister Spring (i.e., large standard deviations), the dilutions predicted using contaminant concentrations are similar to those predicted using the above volumetric water-balance approach.

Once in the springs, aside from the processes of dilution and dispersion, any TCE would volatilize, nitrate could be taken up by plants on the edge of the springs, nitroaromatic compounds would photolyze, and uranium would undergo similar processes in the springs as in groundwater. This degradation is evident from monitoring data obtained from the springs and downstream reaches, including Burgermeister Spring; all COCs other than uranium have been reported at concentrations lower than the PRGs established for groundwater and much lower than concentrations measured in the chemical plant area. Uranium concentrations have been reported at slightly higher levels than the current maximum concentrations reported for the monitoring wells because of residuals in fractured zones.

Any discharge water that is not evaporated or used by plants flows into Lake 34, which provides additional dilution and discharge water to Dardenne Creek. This creek provides a natural hydrogeologic boundary between watersheds and is the northernmost boundary for water originating in the chemical plant area.

Tables 7 and 9 list the relevant physical parameters that were used for calculating remediation times for each of the seven zones and COCs. Table 10 lists the number of pore volumes of contaminated water that must be removed from each zone in order to attain the desired cleanup goals. In each case, an effective porosity of 0.28 and a bulk density of 1.7 g/cm^3 were used. Table 10 also lists the associated maximum and minimum cleanup times calculated for the seven zones and COCs on the basis of a hydraulic gradient of 0.01. Cleanup times in zones that have a high conductivity (e.g., Zone 5) are relatively short; cleanup times in zones that have a low hydraulic conductivity (e.g., Zone 3) can be very long.

TABLE 9 Chemical and Transport Parameters Used for Contamination Zone Calculations

Parameter	TCE	Uranium	Nitrate	2,4-DNT	2,6-DNT	2,4,6-TNT	1,3,5-TNB
K_d (mL/g)	0.3	5	0.5	0.63	1.29	0.28	0.15
R	2.8	31.4	4.0	4.8	8.8	2.7	1.9

2.3 DETAILED ANALYSIS OF ALTERNATIVE 3: MONITORED NATURAL ATTENUATION

The activities associated with Alternative 3 include the following:

- Monitoring of groundwater to verify performance of natural processes in attenuating contaminant concentrations, and
- Construction and operation of potential additional monitoring wells.

Alternative 3 would involve continued monitoring. A sampling and analytical scheme would be implemented to verify that the natural attenuation processes of dilution and dispersion were occurring. Sampling of groundwater and springs would be performed to track the direction and rate of movement of the contaminated groundwater as a function of time.

Groundwater monitoring would be conducted using the existing well network, as appropriate. This network could be expanded or reduced, depending on the results of future efforts to optimize the network for long-term monitoring to support MNA as a remedial option.

For the evaluation (e.g., costing purposes) of Alternative 3, it was assumed that additional monitoring wells, equivalent to approximately 25% of the number of existing wells, would be installed and operated. The exact monitoring network and details regarding frequency of sampling and parameters analyzed would be identified in subsequent remedial design/remedial action (RD/RA) reports in coordination with the EPA and the Missouri Department of Natural Resources.

TABLE 10 Estimated Pore Volumes and Cleanup Times for Monitored Natural Attenuation

	Zone 1		Zone 2		Zone 3		Zone 4		Zone 5		Zone 6		Zone 7	
Contaminants	No. of Pore Volumes	Cleanup Time (yr)	No. of Pore Volumes	Cleanup Time (yr)	No. of Pore Volumes	Cleanup Time (yr)	No. of Pore Volumes	Cleanup Time (yr)	No. of Pore Volumes	Cleanup Time (yr)	No. of Pore Volumes	Cleanup Time (yr)	No. of Pore Volumes	Cleanup Time (yr)
TCE	6.6 – 15.8	61 – 145	0.3	14	NA[a]	NA	NA	NA	NA	NA	NA	NA	NA	NA
Uranium	43	395	NA	NA	2.2 – 14.2	2,400 – 15,460	NA	NA	NA	NA	NA	NA	11.2	6,530
Nitrate	8.7 – 18.4	80 – 169	3.3 – 15.2	149 – 685	8.3 – 14.9	9,040 – 16,220	NA	NA	9.4	3	NA	NA	NA	NA
2,4-DNT	9.1 – 12.2	84 – 112	0.8	36	0.4 – 9.1	435 – 9,910	0.4 – 19.2	10 – 480	NA	NA	NA	NA	NA	NA
2,6-DNT	5.4 – 6.4	50 – 59	25.3 – 26	1,140 – 1,172	3.3 – 25.7	3,600 – 27,980	11.9 – 59.3	300 – 1,480	20.3	7	16.3	7,600	NA	NA
2,4,6-TNT	NA	NA	NA	NA	NA	NA	24.1	602	1.2	0.4	NA	NA	NA	NA
1,3,5-TNB	NA	NA	4.7 – 6.7	212 – 302	NA	NA	0.8 – 7.6	20 – 190	0.2	0.1	2.6	1,210	NA	NA

[a] NA = not applicable.

This assessment assumed that monitoring would continue until groundwater concentrations at the chemical plant area attained PRGs or reference points. Standard operating procedures used for current monitoring activities would be expected to be adopted for this monitoring effort. Water levels would be measured during each sampling event; quality assurance/quality control samples would be collected during each sampling event, as appropriate. For this analysis, it was assumed that the frequency of sampling would be annual because of the low groundwater velocities and the stability of the contaminated zones, observed to date.

Periodic maintenance of the groundwater monitoring wells and dedicated sampling equipment would be expected to extend the life of the equipment. Monitoring wells would be evaluated with regard to performance and condition and integrity of various well components such as concrete pads, posts, and protective casings. Periodic inspections to determine the need for maintenance would be guided by the collection and analysis of representative groundwater samples. After the completion of long-term monitoring activities, the monitoring wells would be managed consistent with current project practices (e.g., plugged and abandoned).

Institutional controls that might be applied to the chemical plant area groundwater include land use restrictions. Land use restrictions could include St. Charles County zoning regulations and deed restrictions by the Missouri Department of Conservation on land not currently under federal ownership (e.g., August A. Busch Memorial Conservation Area). Deed restrictions would involve specific limitations on future land use that are incorporated in the deed of ownership to the property. Such restrictions would prevent activities that could cause direct exposure or releases of groundwater contaminants. Deed restrictions accompany the deed to the property in a manner that is generally binding and must be transferred to all subsequent owners of the property. Examples of deed restrictions include those prohibiting residential or agricultural use. Drilling for mineral, water, or other purposes would also be prohibited.

Continued federal ownership of the area containing the on-site disposal cell at the chemical plant area by the DOE is certain. The federal government will continue to control this area, with the intention of restricting site development activities through the rights of ownership. On-property development activities, such as agricultural or residential use, could be restricted or prohibited by the federal government which, as the property owner, would retain all rights to preclude these

activities. Monitoring would provide information on contaminant concentrations indicating the need for maintaining or implementing institutional controls.

Because contaminants would remain in site groundwater at concentrations above levels that allow for unlimited use and unrestricted exposure, reviews would be conducted at least every five years as required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). If monitoring showed that the level of contaminants in the groundwater had decreased significantly during the prior five-year period, the number of wells sampled and the sampling frequency might be reduced. Wells that duplicated information, provided unreliable information (e.g., wells that were dry part of the year), or yielded samples containing groundwater concentrations below the PRGs for all contaminants might be considered for elimination. The number of monitoring wells and sampling frequency would be determined in collaboration with the regulators.

2.3.1 Overall Protection of Human Health and the Environment

Alternative 3 would be adequately protective of human health and the environment over the long term. Migration of the contamination toward the surface springs would be monitored. Data collected from monitoring would be used to verify and ensure continued protection of human health and the environment.

Restoration of the shallow bedrock aquifer could be provided by existing natural processes (i.e., dilution and dispersion) that are expected to attenuate contaminant concentrations.

Alternative 3 is not expected to result in any unacceptable impacts to human health or the environment during implementation.

2.3.2 Compliance with Potential ARARs

Chemical-specific ARARs (MCLs) have been identified for nitrate (10 mg/L), TCE (5 μg/L), and three nitroaromatic compounds (nitrobenzene at 17 μg/L, 2,4-DNT at 0.11 μg/L, and 1,3-TNB at 1.0 μg/L). The current levels of nitrate, TCE, and 2,4-DNT in groundwater at the chemical plant exceed the respective chemical-specific ARARs. Alternative 3 would meet chemical-specific ARARs.

2.3.3 Long-Term Effectiveness and Permanence

Alternative 3 would afford long-term effectiveness and performance because contaminant concentrations would have attenuated to levels equivalent to PRGs. After the PRGs have been attained, the groundwater at the chemical plant area would, therefore, not pose any unacceptable risk to human health and the environment. And no new contamination should be introduced into the groundwater because source removals are expected to prevent this occurrence.

2.3.4 Reduction of Toxicity, Mobility, or Volume through Treatment

There would be no reduction of toxicity, mobility, or volume through treatment because this alternative does not involve treatment of the contaminated groundwater. Contaminant concentrations at the chemical plant area would decrease with time as the result of source removal and infiltration from rainwater and runoff. Therefore, reduction of toxicity and volume would be achieved through natural means.

2.3.5 Short-Term Effectiveness

The potential short-term environmental impacts associated with Alternative 3 are minimal. Potential risks to workers would result primarily from physical hazards during construction activities associated with the construction of the potential additional monitoring wells. Those construction activities are estimated to result in less than one case of occupational injury and no occupational fatalities. This estimate is based on industry-specific statistics from the U.S. Bureau of Labor Statistics, as reported by the National Safety Council (1995). Physical hazards would be minimized by adherence to stringent health and safety protocols.

Minimal short-term impacts are expected as a result of noise, exhaust fumes, and dust associated with any construction of new monitoring wells. Potential impacts to biological resources would be mitigated by avoiding unnecessary damage to vegetation, wildlife, and soil through controlling traffic and minimizing the area of disturbance.

2.3.6 Implementability

Implementation of MNA requires a clear understanding of the specific processes that lead to decreasing contaminant availability and concentrations. The specific processes need to be identified and quantified to the extent that their long-term reliability can be assured.

Site operations would continue to use readily available resources for monitoring and maintaining institutional controls. Construction of any new monitoring wells would simply require mobilization of a drilling rig for installation and acquisition of well materials for construction. Resources required for maintenance of existing and proposed groundwater monitoring systems would also be readily available. Minimal administrative complexities would be associated with monitoring well installation.

Groundwater monitoring would be readily implementable. No special equipment or personnel would be required to implement groundwater monitoring other than that presently used. Numerous wells currently exist at the chemical plant area, and additional wells could be easily installed and monitored. Monitoring of contaminant zone migration would be relatively easy to implement. Implementation of institutional controls on properties that are not federally owned would require reaching agreement with the appropriate property owners.

The administrative feasibility of this alternative would be relatively straightforward. Remedial activities at the Weldon Spring site are coordinated with the State of Missouri and EPA Region VII. That coordination would continue during the implementation of Alternative 3, and no additional coordination for monitoring activities would be required with any other agencies beyond that already occurring. No permit or license for on-site activities would be required.

2.3.7 Cost

Costs for Alternative 3 would be associated with continuing the existing environmental monitoring program and constructing and operating possible new monitoring wells. Feasibility-level cost estimates were prepared using standard cost-estimating sources of the *Unit Price Book* developed by the U.S. Army Corps of Engineers (1989). A cost differential was included to account for the differences in material and labor costs for the Weldon Spring site, as compared with the generic *Unit Price Book* costs.

The estimated total costs for Alternative 3 are given in Table 11; annual costs are estimated to be approximately $0.3 million.

The capital cost for the construction of the potential additional monitoring wells (15 assumed) for Alternative 3 is estimated to be approximately $0.3 million. Replacement costs are projected to range between $2 and $10 million, assuming monitoring well replacement every 50 years (the monitoring time of the various zones within the chemical plant area extend past the assumed 50-year service life of the monitoring equipment). The cost of groundwater monitoring at the chemical plant area would range between $132 and $1,800 million. The present worth of Alternative 3 is estimated to range between $3 million and $4 million.

TABLE 11 Cost Estimate for Alternative 3[a]

Zone	Estimated Cost ($)						
	Groundwater Monitoring Well Construction[b]	Groundwater Monitoring[c]		Groundwater Monitoring Well Replacement[c,d]		Total[c]	
1	$52,000	$3,086,000	$24,376,000	$17,000	$120,000	$3,155,000	$24,548,000
	($52,000)	($852,000)	($882,000)	($0)	($88,000)	($904,000)	($1,022,000)
2	$35,000	$480,000	$40,181,000	$0	$395,000	$515,000	$40,611,000
	($35,000)	($300,000)	($490,000)	($0)	($49,000)	($335,000)	($574,000)
3	$35,000	$22,371,000	$1,438,922,000	$137,000	$9,604,000	$22,543,000	$1,448,561,000
	($35,000)	($735,000)	($735,000)	($74,000)	($74,000)	($844,000)	($844,000)
4	$35,000	$480,000	$71,038,000	$0	$498,000	$515,000	$71,571,000
	($35,000)	($337,000)	($686,000)	($0)	($69,000)	($372,000)	($790,000)
5	$35,000	$1,000	$96,000	$0	$0	$36,000	$131,000
	($35,000)	($1,000)	($74,000)	($0)	($0)	($36,000)	($109,000)
6	$35,000	$16,594,000	$104,225,000	$412,000	$2,612,000	$17,041,000	$106,872,000
	($35,000)	($196,000)	($196,000)	($20,000)	($20,000)	($251,000)	($251,000)
7	$35,000	$89,551,000	$89,551,000	$2,234,000	$2,234,000	$91,820,000	$91,820,000
	($35,000)	($196,000)	($196,000)	($20,000)	($20,000)	($251,000)	($251,000)
Total	$262,000	$132,563,000	$1,768,389,000	$2,800,000	$15,463,000	$135,625,000	$1,784,114,000
	($262,000)	($2,617,000)	($3,259,000)	($114,000)	($320,000)	($2,993,000)	($3,841,000)

a Costs presented include all major costs over the entire duration of Alternative 3. Costs in parentheses are present-worth estimates.

b Considered capital costs.

c Minimum and maximum costs are presented as follows:

Zone 1: minimum duration due to 2,6-DNT (50 years), maximum duration due to uranium (395 years).
Zone 2: minimum duration due to TCE (14 years), maximum duration due to 2,6-DNT (1,172 years).
Zone 3: minimum duration due to 2,4-DNT (435 years), maximum duration due to 2,6-DNT (27,980 years).
Zone 4: minimum duration due to 2,4-DNT (10 years), maximum duration due to 2,6-DNT (1,480 years).
Zone 5: minimum duration due to 1,3,5-trinitrobenzene (1,3,5-TNB) (0.1 years), maximum duration due to 2,6-DNT (7 years).
Zone 6: minimum duration due to 1,3,5-TNB (1,210 years), maximum duration due to 2,6-DNT (7,600 years).
Zone 7: minimum and maximum duration due to uranium (6,530 years).

d Costs assume a 50-year replacement period for on-site monitoring wells and associated equipment.

3 EVALUATION OF ALTERNATIVE 4: GROUNDWATER REMOVAL AND ON-SITE TREATMENT USING GRANULAR ACTIVATED CARBON

To support the analysis presented in the FS (DOE and DA 1998) for Alternatives 4 and 7, contaminated zones were identified within the chemical plant area aquifer. The various zones identified were presented in Appendix C of the FS. For this supplement, the zone determinations were reviewed and revised as needed in order to be inclusive of all contaminated areas within the chemical plant aquifer of concern. Groundwater data reported for 1997 to 1998 were used in the evaluation, as discussed in Chapter 1.

Calculations for each zone were performed to determine the number of extraction wells, the pore volumes, and required cleanup times to attain PRGs. The methodology for these calculations is discussed in Section 3.1. A detailed analysis of Alternative 4 is presented in Section 3.2. The results of the calculations discussed in Section 3.1 were used in the evaluation presented in Section 3.2.

3.1 METHODOLOGY

As a general rule, increasing the number of extraction wells reduces the time required to achieve cleanup criteria. However, the properties of the shallow groundwater aquifer at the chemical plant area limit the maximum number of wells that can be used for pump and treat (i.e., if too many extraction wells are operating, the aquifer may dewater). An optimum number of pump and treat wells can, in principle, be calculated for a groundwater system by using the properties of the aquifer and a time or cost constraint. For the present calculations, a minimum number of extraction wells was calculated with a method developed by Javandel and Tsang (1986). This same method was used in the FS (DOE and DA 1998) to estimate the number of extraction wells needed at the chemical plant area. A number of collinear wells were assumed to have been installed perpendicular to the direction of groundwater flow near the downgradient edge of a zone of contamination. These wells form a capture zone that removes contaminated groundwater across the full width and depth of the contaminated zone. Because these wells are located at the downgradient edge of the contamination zone, cleanup times are conservatively long. Cleanup times can be decreased by installing additional wells in the interior of the contaminated zone or at localized "hot spots."

If higher levels of residual contamination (i.e., concentrations greater than PRGs) were acceptable, shorter cleanup times could also be obtained. For example, if pump and treat were implemented in Zone 1 for TCE for a period of 10 years, the residual concentration would be reduced by almost 60% (i.e., the residual TCE concentration would be 40% of its initial value). The time-dependent residual contaminant levels for the seven zones and COCs are discussed further in Appendix A.

With the Javandel and Tsang (1986) method, the number of extraction wells needed to capture a "plume," or in this case, the zones of contamination, is given by the expression

$$n = \frac{2t\nabla hKW}{Q}, \tag{2.7}$$

where

K = hydraulic conductivity,

Q = sustainable pumping rate that produces drawdown over the thickness of the contaminated zone,

t = thickness of the contaminated zone,

W = width of the contaminated zone, and

∇h = hydraulic gradient present in the shallow groundwater aquifer.

Table 8 provides physical descriptions of the seven contaminated zones (including width and average hydraulic conductivity. Table 12 lists the estimated sustainable pump rates and the number of extraction wells that would be needed for each zone.

If the number of extractions wells needed is known, the cleanup time for reducing the concentration of the contaminant from an initial value to a specific PRG can be calculated. For a nondegrading contaminant (i.e., one that does not decay, chemically react, or precipitate out of

TABLE 12 Estimated Pore Volumes and Cleanup Times for Pump and Treat Method

	Zone 1				Zone 2				Zone 3				Zone 4			
Contaminants	No. of Extraction Wells	Pump Rate	No. of Pore Volumes	Cleanup Time (yr)	No. of Extraction Wells	Pump Rate	No. of Pore Volumes	Cleanup Time (yr)	No. of Extraction Wells	Pump Rate	No. of Pore Volumes	Cleanup Time (yr)	No. of Extraction Wells	Pump Rate	No. of Pore Volumes	Cleanup Time (yr)
TCE	5	1	6.6 – 15.8	30 – 71	10	0.3	0.3	7	2	0.3	NA	NA	3	3	NA	NA
Uranium	5	1	43	194	10	0.3	NA[a]	NA	2	0.3	2.2 – 14.2	995 – 6,425	3	3	NA	NA
Nitrate	5	1	8.7 – 18.4	39 – 83	10	0.3	3.3 – 15.2	72 – 330	2	0.3	8.3 – 14.9	3,755 – 6,740	3	3	NA	NA
2,4-DNT	5	1	9.1 – 12.2	41 – 55	10	0.3	0.8	18	2	0.3	0.4 – 9.1	180 – 4,100	3	3	0.4 – 19.2	5 – 229
2,6-DNT	5	1	5.4 – 6.4	24 – 29	10	0.3	25.3 – 26	550 – 570	2	0.3	3.3 – 25.7	1,490 – 11,630	3	3	11.9 – 59.3	142 – 710
2,4,6-TNT	5	1	NA	NA	10	0.3	NA	NA	2	0.3	NA	NA	3	3	24.1	287
1,3,5-TNB	5	1	NA	NA	10	0.3	4.7 – 6.7	100 – 150	2	0.3	NA	NA	3	3	0.8 – 7.6	10 – 90

	Zone 5				Zone 6				Zone 7			
Contaminants	No. of Extraction Wells	Pump Rate	No. of Pore Volumes	Cleanup Time (yr)	No. of Extraction Wells	Pump Rate	No. of Pore Volumes	Cleanup Time (yr)	No. of Extraction Wells	Pump Rate	No. of Pore Volumes	Cleanup Time (yr)
TCE	2	10	NA	NA	1	0.3	NA	NA	1	0.3	NA	NA
Uranium	2	10	NA	NA	1	0.3	NA	NA	1	0.3	11.2	1,220
Nitrate	2	10	9.4	9	1	0.3	NA	NA	1	0.3	NA	NA
2,4-DNT	2	10	NA	NA	1	0.3	NA	NA	1	0.3	NA	NA
2,6-DNT	2	10	20.3	20	1	0.3	16.3	2,240	1	0.3	NA	NA
2,4,6-TNT	2	10	1.2	1	1	0.3	NA	NA	1	0.3	NA	NA
1,3,5-TNB	2	10	0.2	0.2	1	0.3	2.6	360	1	0.3	NA	NA

[a] NA = not applicable because the particular COC has not been reported at concentrations greater than the PRGs.

solution), the number of pore volumes of groundwater that must be removed to achieve a cleanup goal is given by the following empirical relation (Cohen et al. 1997):

$$Number\ of\ pore\ volumes = R ln \frac{C_0}{C_w}, \tag{2.8}$$

where R is the retardation coefficient for the contaminant, C_0 is its initial concentration, and C_w is its PRG.

The retardation coefficient is given by the relationship:

$$R = 1 + \frac{\rho_b K_d}{\phi}, \tag{2.9}$$

where K_d is the contaminant's distribution coefficient (mL/g), and ρ_b is the bulk density of the porous medium (Freeze and Cherry 1979).

A single pore volume for the contaminated zones was estimated as the volume of a parallelepiped that has a width (W), thickness (t), length parallel to the direction of groundwater flow (L), and an effective porosity (ϕ). This volume is given by the following relationship:

$$Pore\ volume = LWt\phi\ . \tag{2.10}$$

An approximate cleanup time for a contaminant is then found with the following equation:

$$\Delta t = \frac{R ln(\frac{C_0}{C_w}) LWt\phi}{nQ}\ .$$

Table 9 lists the chemical and transport properties for the COCs for the seven contaminated zones. Table 12 presents two ranges; one for the number of pore volumes and one for the cleanup time required to achieve cleanup goals for each zone. For both ranges, the lower end of the range was derived from the lowest maximum contaminant concentration in the zone; the higher end of the

range was derived from the highest maximum value. By using the lowest maximum and the highest maximum concentration values, cleanup times for each COC and for each zone can be bracketed.

Pump and treat cleanup times are greatest for those zones that require the removal of the largest numbers of pore volumes of contaminated water with the least number of extraction wells (e.g., cleanup of 2,6-DNT in Zone 3 is estimated to take between 1,490 and 11,630 years). As stated previously, this remediation time could be reduced by installing additional wells within the contaminated zone. For the mass-balance approach used, doubling the number of wells would reduce the cleanup time by a factor of two. However, the physical attributes of the shallow groundwater aquifer beneath the chemical plant area will ultimately limit the number of wells that can be installed and pumped at the specified rates. If too many wells are installed, the aquifer would be dewatered and a modified pumping schedule (i.e., turning the pumps on and off to permit the aquifer to recover) would have to be implemented, or the number of wells would need to be reduced. Either of these strategies could increase the predicted cleanup times greatly. In addition, the design of an optimized pump and treat system would have to incorporate the spatial heterogeneity of the shallow groundwater aquifer. This heterogeneity would be best accommodated by installing a pump and treat system using a phased approach that would permit modification of the design as new information from the field is acquired.

3.2 DETAILED ANALYSIS OF ALTERNATIVE 4: GROUNDWATER REMOVAL AND ON-SITE TREATMENT USING GRANULAR ACTIVATED CARBON AND ION EXCHANGE

The activities associated with Alternative 4 include the following:

- Extraction and ex-situ treatment of the groundwater at the chemical plant area to attain PRGs for groundwater, and
- Environmental monitoring at the site to ensure performance of the remedy.

This alternative involves using conventional vertical extraction wells to remove groundwater with contaminant levels exceeding PRGs and reference points (for uranium), pumping and treating the groundwater at an aboveground treatment system, and releasing or managing the treated groundwater consistent with overall site strategies. Adsorption by GAC, which is a well-

developed, effective, and widely applied technology, would be used to remove organic materials, including nitroaromatic compounds and TCE by chemically and physically binding them to the carbon. Ion exchange would be used to treat nitrate and uranium. Groundwater treatment residuals such as spent GAC would be transported off-site for disposal.

Approximately 24 vertical extraction wells at the chemical plant area (see Section 2.1) were estimated to be required to achieve a reasonable extraction rate for all the zones of contamination discussed in Chapter 1. This number of wells would provide wide enough coverage to minimize any bypass of groundwater contaminated above the PRGs and the reference points for uranium.

The extracted groundwater would be contained in an aboveground tank prior to being conveyed through pipes to the treatment facility. A pipeline would be constructed connecting the discharge of the aboveground tank with the groundwater treatment facility.

A single groundwater treatment facility was assumed to be constructed with a treatment capacity on the order of 315 L/min (83 gpm). (This analysis assumed that a permanent structure would be necessary, given the estimated treatment duration.) The facility footprint would be on the order of 220 m^2 (2,400 ft^2). The groundwater treatment facility would be a single-story metal frame general use structure housing the groundwater treatment system, water storage tanks, pumps, and associated equipment.

The conceptual groundwater treatment process would involve clarification and multimedia filtration to remove any solids collected during groundwater extraction, liquid phase adsorption using GAC to remove TCE and nitroaromatic compounds, and reverse osmosis and ion exchange for nitrate and uranium. The process itself is similar to that currently applied by the Site Water Treatment Plant (SWTP) at the chemical plant to treat contaminated surface water.

The extracted groundwater would first be sent to a feed tank to dampen variations in flow and groundwater quality among the 24 extraction wells, thereby providing equalization of influent. The tank would also receive recycled water from dewatering (i.e., the filter press). Uranium and other metals would be removed within the mix tank by precipitation. Several precipitation additives are available. Although lime is the most common precipitant in use, it tends to be inefficient because of the volume of sludge produced. This analysis assumes the use of lime; an additive (or combination

of additives) would be selected during the RD/RA phase on the basis of cost and the volume of sludge produced. Influent pH adjustment may not be necessary, although it could easily be added to the system if necessary.

Following precipitation, the precipitate would be rapidly transferred to the clarifier, where the solids in the precipitate mixture would settle to the bottom. Sludges from the clarifier, containing the solids and precipitated uranium and other metals, would be dewatered using a filter press. This type of filter press can usually achieve greater than 50% solids in the filter cake. The solid sludge would be sent for off-site disposal.

Clarifiers are generally sufficient for removing suspended solids. However, because solids from precipitation or filter backwash sometimes coagulate and settle poorly, multimedia filters would be included to remove any fine particles that did not settle out in the clarifier. If the solids from precipitation coagulate and settle poorly, the filter columns would be sized to handle the additional solids loading. Filtration would be needed to prevent fouling or plugging of the GAC. Two columns in parallel would be used; one column would be on line while the other column was being backflushed with treated groundwater.

Granular activated carbon would be used to remove organic materials (nitroaromatic compounds and TCE) by chemically and physically binding them to the carbon. In liquid-phase carbon adsorption, the groundwater would be passed through a series of packed bed adsorbers containing the activated carbon. The activated carbon selectively adsorbs organic compounds, which are attracted to and held in the internal micropores of carbon granules. This analysis assumed the use of downflow fixed-bed GAC adsorbers, because they constitute a cost-effective treatment technology that provides the lowest effluent concentrations compared with other carbon adsorber designs.

Ionic species such as nitrates would be removed by means of reverse osmosis, which involves forcing the contaminated water across a semipermeable membrane, which reduces the mineral content in the groundwater, thereby removing nitrate. Treatment by reverse osmosis would result in a permeative stream with low concentrations of ions and a low-volume reject stream containing the concentrated dissolved compounds. This reject stream would be sent to an evaporator for further concentration. The evaporator concentrate would be dewatered using a filter press and then mixed with cement additives to produce a solidified residue (grout) for disposal.

Ion exchange would be used to remove trace amounts of uranium and nitrate from the groundwater; this method has been widely applied for the treatment of high flows of wastewater with dilute concentrations of metals. In ion exchange, the contaminants are exchanged with ions of the resins (e.g., sodium [Na^+]). The effluent from the reverse osmosis would pass through two ion-exchange columns in series. The system would include a third column, which would allow two-column operation while one column was being regenerated. The ion-exchange columns would be regenerated with acidic, basis, or salt solutions (depending on the resin used). For example, a solution of sodium chloride and soda ash is used for regeneration of ion-exchange systems used in mining uranium.

Series operation of the ion-exchange columns would allow maximum resin loading and provide a safety factor against off-specification effluent. Water quality would be monitored after the first column, as well as after the second. When breakthrough (rapidly rising contaminant concentrations) was observed in the first column, the third (fresh) column would be placed on line. This would allow the first column to be run to exhaustion without any danger of exceeding effluent specifications. When the first column was exhausted, it would be taken off-line and regenerated. After regeneration, it would become the new third column. This operation would allow more efficient regeneration, which would lower costs. The third column would also provide a backup in the event that one column required maintenance. The treated water from the ion-exchange resins would be chemically analyzed to verify that the water had been treated to acceptable levels for discharge.

The system described for this alternative should be effective for removing TCE, nitrate, nitroaromatic compounds, and uranium. Other treatment processes or system configurations could be used, provided they are capable of cost effectively achieving the required effluent concentrations. In general, the removal characteristics of any particular combination of contaminants in a waste stream are not predictable. A pilot test using a sample of the affected groundwater under conditions comparable to those of the chemical plant might be required to accurately determine the optimal process and its characteristics. The actual design for treatment of the extracted groundwater would be determined during the remedial design phase, at which time the necessary flow capacity, required

ontact time to reduce contaminant concentrations, and contaminant concentrations likely to be encountered would be taken into account.

It was assumed that any sludge generated by groundwater treatment would be managed similarly to sludge generated by the water treatment process at the SWTP. This sludge would be allowed to dewater.

The dewatered sludge would be packaged for off-site treatment and disposal. If the waste-acceptance criteria for off-site disposal are met, the dewatered sludge would be shipped via truck to an off-site disposal facility (transport by rail does not appear to be an option because of the lack of a nearby railhead for shipping). Assuming packaging in a standard 55-gal (208-L) drum and truck transport, only two off-site shipments of dewatered sludge to an appropriate disposal facility would be required annually.

If necessary to meet the waste acceptance criteria for off-site disposal, the sludge would be properly treated prior to disposal. Most of the solids in the sludge would be uncontaminated dissolved solids such as calcium carbonates and hydroxides. Radioactive contaminants would be present in relatively low concentrations.

The replacement schedule for spent GAC would depend on its adsorption efficiency under actual operating conditions. It was assumed that the spent carbon would be replaced every three months. The spent carbon would then be regenerated at the supplier facility or sent to a commercial disposal facility. Because a process for off-site thermal regeneration of GAC contaminated with explosives is currently under development, this analysis assumed disposal of the spent contaminated carbon. For a carbon fill of 400 kg (880 lb), the amount of spent carbon to be disposed of annually as hazardous waste would be approximately 1,600 kg (3,500 lb). Assuming packaging in standard 55-gal (208-L) drums and truck transport, less than one shipment to an appropriate disposal facility would be required annually. On the basis of literature values of carbon adsorption capacity for various compounds, the spent carbon would contain approximately 2 wt% contaminant (primarily TCE and 1,3,5-TNB).

After construction of the extraction well network and associated groundwater treatment system, the two systems would be carefully monitored on a regular basis and their performance

would be evaluated. The actual performance in the field may vary from that assumed during design, given uncertainties about subsurface geology prior to construction and operation.

Because contaminants would remain in site groundwater at concentrations above levels that allow for unlimited use and unrestricted exposure, reviews would be conducted at least every five years per CERCLA.

3.2.1 Overall Protection of Human Health and the Environment

Alternative 4 would be protective of human health and the environment because contaminated groundwater would be extracted or removed and then treated under this alternative. After PRGs are attained, the groundwater quality would be amenable for unrestricted use. Source removals conducted per the chemical plant ROD (DOE 1993) should prevent the introduction of any new contamination to the groundwater. Minimal disturbance or impact to environmental resources in the area is expected during and after implementation.

3.2.2 Compliance with Potential ARARs

Potential regulatory requirements that might be applicable or relevant and appropriate to the final remedial action alternatives are identified and evaluated in Appendix A of the FS (DOE and DA 1998). Chemical-specific ARARs (MCLs) have been identified for nitrate (10 mg/L), TCE (5 µg/L), and three nitroaromatic compounds (nitrobenzene at 17 µg/L, 2,4-DNT at 0.11 µg/L, and 1,3-TNB at 1.0 µg/L). The current levels of nitrate, TCE, and 2,4-DNT in groundwater at the chemical plant exceed the respective chemical-specific ARARs for constituents found in groundwater. Compliance with chemical-specific ARARs is achieved by the removal and treatment of groundwater contaminated above the ARARs.

3.2.3 Long-Term Effectiveness and Permanence

Alternative 4 would afford long-term effectiveness and performance because it would reduce all contaminant concentrations through extraction and treatment of contaminated groundwater within the shallow bedrock aquifer to attain PRGs. This alternative would provide for the reduction or elimination (to below the acceptable risk range of 10^{-6} to 10^{-4} and a hazard index of 1) of

potential risk associated with residential use of chemical plant groundwater. Treatment waste (such as spent GAC) would be disposed of at an appropriate off-site facility.

3.2.4 Reduction of Toxicity, Mobility, or Volume through Treatment

Alternative 4 would satisfy the statutory preference for treatment as a principal element of remediation and would reduce the toxicity, mobility, or volume of the contaminated groundwater through treatment. Alternative 4 would reduce mobility by hydraulically controlling migration of contaminated groundwater at the chemical plant area through extraction of groundwater. The toxicity of TCE and other organic contaminants removed by GAC would be minimized by subsequent treatment and disposal at an approved disposal facility. The toxicity of nitrates and uranium would be similarly minimized. Successful implementation of Alternative 4 would reduce the toxicity, mobility, or volume associated with all contaminants in groundwater within the shallow bedrock aquifer.

3.2.5 Short-Term Effectiveness

Risks to workers would result primarily from physical hazards during construction activities associated with the construction of extraction wells and treatment facilities. Those construction activities are estimated to result in approximately 7 cases of occupational injury, assuming construction of the 24 vertical extraction wells and the associated groundwater treatment facility at the chemical plant area. No occupational fatalities are expected to occur. This estimate is based on industry-specific statistics from the U.S. Bureau of Labor Statistics, as reported by the National Safety Council (1995). Physical hazards would be minimized by adherence to stringent health and safety protocols.

Minimal environmental impacts would result from construction of the extraction well network and associated groundwater treatment facility at the chemical plant area. The primary impact to the environment would be associated with installation of the 24 extraction wells at the chemical plant area. These activities may result in physical disturbances of the habitat, but these would be of short duration. Some short-term impacts might occur as a result of noise, exhaust fumes, and dust associated with any construction activities. Impacts to biological resources would be mitigated by

avoiding unnecessary damage to vegetation, wildlife, and soil through controlling traffic and minimizing the area of disturbance.

3.2.6 Implementability

Significant uncertainty in the implementability of Alternative 4 is associated with the need for site (area)-specific hydrogeologic data to verify the appropriateness of assumptions used in the evaluations. One possible problem considered is the potential for the groundwater extraction system to not achieve the design flow rates for a single extraction well for the various zones assumed in Section 3.1. If area-specific flow rates vary from those shown in Section 3.1, performance of this alternative would vary accordingly. This situation could result in schedule delays and unsuccessful implementation of this alternative.

Another uncertainty is the potential dewatering of the shallow bedrock aquifer during groundwater extraction. Groundwater monitoring at the chemical plant area indicated that almost all of the monitoring wells pump dry during low rates of purging. Slow and incomplete water level recovery were observed during a recent pumping test at the chemical plant area. The possibility of semipermanently dewatering the shallow bedrock aquifer in the vicinity of the TCE-contaminated zone was stated to pose a potential obstacle to long-term continuous pumping (MK-Ferguson 1998).

Construction of the vertical extraction wells would require mobilization of a drilling rig (or several) for installation. Minimal administrative complexities would be associated with extraction well installation.

Few implementability concerns associated with the groundwater extraction and treatment technologies would be posed by Alternative 4. Because groundwater extraction and treatment are well developed technologies, technical problems are not likely to cause significant delays. Site operations would continue to use readily available resources for monitoring. Discharge of treated groundwater would likely require coordination with regulatory agencies such as the EPA and the Missouri Department of Natural Resources.

Groundwater treatment services are commercially available, and equipment and specialists are available within DOE and private industry. The groundwater treatment technologies considered for Alternative 4 are well developed and have proven effective in SWTP operations. They are

frequently used in water treatment applications, and the equipment is readily available. Further development of these technologies would not be required before they could be applied at the site. The treatment itself is relatively simple and can be implemented with a high degree of operating confidence.

Building construction would follow generally accepted designs and would not require unusual construction or unique construction equipment. No unusual contractor or supplier requirements appear necessary. The design does not use unusual or rare materials. The building is designed to use standard concrete floors and metal wall construction on spread footings, with at-grade construction. Construction of the building housing the groundwater treatment equipment would not be complicated.

The technical feasibility of secondary waste disposal would be straightforward and reliable. Long-term disposal services would be available (e.g., the projected characteristics of the groundwater treatment residuals appear to fall within the waste acceptance criteria for off-site disposal facilities such as those for Envirocare's disposal facility located approximately 121 km (75 mi) west of Salt Lake City, Utah). Off-site transport of secondary wastes (such as sludge and spent GAC) to commercial disposal sites would consist of a few direct truck transports from the chemical plant to the disposal site.

Groundwater monitoring could be readily implementable. Numerous wells currently exist at the chemical plant, and additional wells could be easily installed and monitored. Monitoring of contaminant zone migration would be relatively easy to implement.

The administrative feasibility of this alternative would be relatively straightforward. Remedial activities at the Weldon Spring site are coordinated with the State of Missouri and EPA Region VII. That coordination would continue during the implementation of Alternative 4, and no additional coordination for monitoring activities would be required with any other agencies beyond that already occurring. No permit or license for on-site activities would be required to conduct groundwater treatment activities.

3.2.7 Cost

Costs for this alternative would be associated with continuing the existing environmental monitoring program and constructing and operating groundwater extraction and treatment systems. Feasibility-level cost estimates were prepared using standard cost-estimating sources of the *Unit Price Book* developed by the U.S. Army Corps of Engineers (1989). A cost differential was included to account for the differences in material and labor costs for the Weldon Spring site, as compared with the generic *Unit Price Book* costs.

Cost estimates for major equipment used in groundwater treatment were obtained from vendors that supplied skid-mounted wastewater treatment modules and by making engineering judgments. Facility costs were estimated on the basis of standard cost engineering references (Means 1994). It was assumed in the development of the costs of the groundwater treatment facility that utilities would be available at the chemical plant, that only tie-ins would be necessary, and that administrative support would be provided by DOE/Weldon Spring Remedial Action Project.

The estimated total costs for Alternative 4 are given in Table 13; annual costs are estimated to be approximately $1.1 million per year. The capital cost of Alternative 4 is estimated to be approximately $7 million. The capital cost would be primarily for installation of the groundwater treatment facility. Replacement costs are projected to range between $410 and $3,900 million, assuming extraction well and groundwater treatment facility replacement every 30 years (the operations duration for remediation of the various zones within the chemical plant area extend past the typical 30-year service life for major equipment). The cost of groundwater monitoring at the chemical plant area would range between $20 million and $397 million. Excluding the decontamination and decommissioning costs of the groundwater treatment facility, the present worth of Alternative 4 is estimated to range between $15 million and $24 million.

TABLE 13 Cost Estimate for Alternative 4[a]

Zone	Estimated Cost ($)								
	Extraction Well and Groundwater Treatment Facility Construction[b]	Extraction Well and Groundwater Treatment Facility Operations[c]		Extraction Well and Groundwater Treatment Facility Replacement[c]		Groundwater Monitoring[c]		Total[c]	
1	$4,245,000	$12,563,000	$101,547,000	$0	$42,384,000	$1,234,000	$9,977,000	$18,042,000	$158,153,000
	($4,245,000)	($6,003,000)	($7,478,000)	($0)	($2,020,000)	($590,000)	($735,000)	($10,838,000)	($14,478,000)
2	$255,000	$220,000	$17,902,000	$0	$134,216,000	$192,000	$15,634,000	$667,000	$168,007,000
	($255,000)	($169,000)	($449,000)	($0)	($121,000)	($148,000)	($392,000)	($572,000)	($1,217,000)
3	$51,000	$1,131,000	$73,051,000	$42,384,000	$2,733,776,000	$8,023,000	$518,348,000	$51,589,000	$3,325,226,000
	($51,000)	($90,000)	($90,000)	($24,000)	($24,000)	($637,000)	($637,000)	($802,000)	($802,000)
4	$764,000	$471,000	$66,895,000	$0	$162,472,000	$206,000	$29,210,000	$1,441,000	$259,341,000
	($764,000)	($386,000)	($1,346,000)	($0)	($364,000)	($169,000)	($588,000)	($1,319,000)	($3,062,000)
5	$1,698,000	$42,000	$4,188,000	$0	$0	$1,000	$137,000	$1,741,000	$6,023,000
	($1,698,000)	($40,000)	($2,218,000)	($0)	($0)	($1,000)	($73,000)	($1,739,000)	($3,989,000)
6	$25,000	$1,131,000	$7,035,000	$84,768,000	$522,738,000	$2,468,000	$15,359,000	$88,392,000	$545,157,000
	($25,000)	($45,000)	($45,000)	($12,000)	($12,000)	($98,000)	($98,000)	($180,000)	($180,000)
7	$25,000	$3,832,000	$3,832,000	$282,561,000	$282,561,000	$8,365,000	$8,365,000	$294,783,000	$294,783,000
	($25,000)	($45,000)	($45,000)	($12,000)	($12,000)	($98,000)	($98,000)	($180,000)	($180,000)
Total	$7,063,000	$19,390,000	$274,450,000	$409,713,000	$3,878,147,000	$20,489,000	$597,030,000	$456,655,000	$4,756,690,000
	($7,063,000)	($6,778,000)	($11,671,000)	($48,000)	($2,553,000)	($1,741,000)	($2,621,000)	($15,630,000)	($23,908,000)

[a] Costs presented include all major costs over the entire duration of Alternative 4. Costs in parentheses are present-worth cost estimates.

[b] Considered capital costs.

[c] Minimum and maximum costs are presented as follows:

Zone 1: minimum duration due to 2,4-DNT (24 years), maximum duration due to uranium (194 years).
Zone 2: minimum duration due to TCE (7 years), maximum duration due to 2,6-DNT (570 years).
Zone 3: minimum duration due to 2,4-DNT (180 years), maximum duration due to 2,6-DNT (11,630 years).
Zone 4: minimum duration due to 2,4-DNT (5 years), maximum duration due to 2,6-DNT (710 years).
Zone 5: minimum duration due to 1,3,5-TNB (0.2 years), maximum duration due to 2,6-DNT (20 years).
Zone 6: minimum duration due to 1,3,5-TNB (360 years), maximum duration due to 2,6-DNT (2,240 years).
Zone 7: minimum and maximum duration due to uranium (1,220 years).

4 ALTERNATE CONCENTRATION LIMITS

The concept of alternate concentration limits (ACLs) provides another approach to setting remediation goals. The NCP (EPA 1990) provides that for Class I and II groundwaters (groundwater at the chemical plant area has been determined to be Class II), ACLs can also be established to set PRGs if certain conditions are met. These conditions include the following: (1) the groundwater must have a known or projected point of entry to surface water; and (2) the remedial action must include enforceable measures that would preclude human exposure to the contaminated groundwater at any point between the facility boundary and all known projected points of entry of such groundwater into the surface water.

As discussed in Section 2.2, dissolved groundwater contaminants in all of the zones of contamination at the chemical plant area have known or projected points of entry to surface water. Zones 1 through 6 would eventually discharge to Burgermeister Spring and other nearby springs. Zone 7 would generally flow toward the Southeast drainage located southeast of the site.

Institutional controls that could be implemented would prevent human exposure to the contaminated groundwater and at the discharge springs. Further, current land use for the site and immediate vicinity does not include groundwater use, and foreseeable future land use would not likely involve groundwater use because municipal water could be made available. In summary, site characteristics appear to meet the conditions required for the consideration of ACLs.

5 SUMMARY

Site data evaluated indicate that after source removal, dilution and dispersion appear to be the primary processes that would further attenuate groundwater contaminant concentrations. On the basis of these attenuation processes, the calculations presented in Chapter 2 indicate that it would take several years to decades (approximately 60 and 7 years respectively, for Zones 1 and 2) for TCE concentrations in Zones 1 and 2 to attenuate to the MCL (or ARAR) of 5 μg/L. For nitrate, the estimates for Zones 1 through 3, where the higher concentrations are clustered, indicate that it would likely take at least 80 years for contaminant concentrations to attenuate to the MCL (or ARAR) of 10 mg/L.

Costs for implementing MNA for groundwater at the chemical plant area are primarily associated with those incurred for monitoring contaminant concentrations and the replacement costs for monitoring wells. Cost estimates are relatively high because a rather lengthy period of monitoring would be involved.

Calculations performed to evaluate the feasibility of groundwater removal and subsequent treatment of the extracted water included determinations for the number of extraction wells needed, required number of pore volumes, and the number of years of implementation required to attain PRGs. The calculations were performed per zone of contamination, as discussed in Chapter 1.

Several observations can be made about the results presented in Chapter 3 regarding Alternative 4. The first is that by looking at the results for Zones 1 and 2 evaluated under Alternative 4, one can also assess the feasibility of Alternative 7, because Alternative 7 addresses this particular subset of Alternative 4 (i.e., Zones 1 and 2). TCE contamination has been observed in Zones 1 and 2, but has not been reported in any of the remaining five zones. Nitrate, nitroaromatic compounds, and uranium have also been reported in Zones 1 and 2. The present-worth costs for implementing the pump and treat alternative in Zones 1 and 2 constitute the major component of the overall present-worth cost for Alternative 4, which indicates that the cost for Alternative 7 would be similarly high. Another observation is that although estimated times are shorter for the pump and treat approach than those for MNA, pump and treat for Zones 1 and 2 likely would take several decades (at least 30 years) to attain ARARs or PRGs. The cost estimates (in present-worth costs)

for Alternatives 4 and 7 are much higher (approximately an order of magnitude higher) than those for Alternative 3.

The comparative analysis table presented in the FS (DOE and DA 1998) has been revised to incorporate the results of the evaluations presented in this supplement. Table 14 summarizes the evaluations against the threshold and balancing criteria for Alternative 3 (MNA) and the six final alternatives presented in the FS (i.e., Alternatives 1, 2, 4, 7, 8, and 9). The information presented in this supplement will be evaluated in conjunction with the information presented in the FS to identify a preferred alternative that will be presented in the Proposed Plan.

TABLE 14 Comparative Analysis of Alternatives

	Alternative 1: No Action	Alternative 2: Long-Term Monitoring	Alternative 3: Monitored Natural Attenuation	Alternative 4: Groundwater Removal and On-Site Treatment Using GAC and Ion Exchange	Alternative 7: Removal and On-Site Treatment of Groundwater (in Zones 1 and 2)	Alternative 8: In-Situ Treatment of TCE Using In-Well Vapor Stripping	Alternative 9: In-Situ Chemical Oxidation of TCE Using Fenton-Like Reagents
Overall protection of human health and the environment	Like all of the alternatives, would be adequately protective of human health and the environment, although monitoring data would not be available to verify this occurrence.	Like all of the alternatives, would be adequately protective of human health and the environment. Monitoring data would be collected to verify that conditions continued to be protective of human health and the environment.	Like all of the alternatives, would be adequately protective of human health and the environment. Monitoring data would be collected to verify that conditions continued to be protective of human health and the environment.	Like all of the alternatives, would be adequately protective of human health and the environment.	Like all of the alternatives, would be adequately protective of human health and the environment.	Like all of the alternatives, would be adequately protective of human health and the environment.	Like all of the alternatives, would be adequately protective of human health and the environment.
Compliance with ARARs	The same as Alternatives 2 and 3. Complies with ARARs; ARARs for TCE, nitrate, and nitroaromatic compounds would be met after a period of time because of source removals performed under the chemical plant ROD (DOE 1993).	Complies with ARARs; similar to Alternatives 1 and 3.	The same as Alternatives 1 and 2; complies with ARARs; calculations indicate a time period of at least several decades for attaining ARARs for TCE, nitrate, and nitroaromatic compounds.	Complies with ARARs; could take several decades (but shorter time period than for Alternative 3) for attaining ARARs.	Complies with ARARs; The ARAR for TCE could be met in a similar amount of time as Alternative 4, but longer than Alternatives 8 and 9. ARARs for nitrate and nitroaromatic compounds would be met in Zones 1 and 2 in a time period similar to that in Alternative 4.	Complies with ARAR for TCE in a shorter period of time than Alternative 7 and in a slightly longer period of time than Alternative 9.	Requires the least time to comply with ARARs for TCE as compared with all other alternatives, including Alternatives 7 and 8.
Long-term effectiveness and permanence	Is expected to afford long-term effectiveness and permanence, although investigative and monitoring activities would not be performed.	Provides for long-term effectiveness and performance; unlike Alternative 1, would provide verification monitoring of the groundwater within the operable unit.	Provides for long-term effectiveness and performance. Verification monitoring data would be collected.	Affords long-term effectiveness and permanence because contaminant concentrations would be removed or reduced through extraction and treatment.	Would reduce concentrations of TCE, nitrate, nitroaromatic compounds and uranium present in Zones 1 and 2. Natural processes and source removals per the chemical plant ROD (DOE 1993) are expected to result in decreases of contaminant levels in the remaining zones.	TCE in Zones 1 and 2 would be reduced or removed by treatment of groundwater. Natural processes and source removals per the chemical plant ROD (DOE 1993) are expected to result in decreases of contaminant levels in the remaining zones.	TCE in Zones 1 and 2 would be reduced or removed. Natural processes and source removals per the chemical plant ROD (DOE 1993) are expected to result in decreases of contaminant levels in the remaining zones.
Reduction of toxicity, mobility, or volume through treatment	Not applicable because the contaminated groundwater would not be treated.	Not applicable because the contaminated groundwater would not be treated.	Not applicable because the contaminated groundwater would not be treated. Restoration of the water-bearing zone within the operable unit would be provided by natural processes, primarily by dispersion and dilution of the contaminated groundwater with uncontaminated groundwater drawn through infiltration of rainwater and runoff.	Reduction of the toxicity, mobility, or volume associated with all groundwater contamination within the shallow bedrock aquifer would be accomplished upon successful implementation of this alternative.	Reduction of the toxicity, mobility, or volume associated with TCE, nitrate, nitroaromatic compounds, and uranium in Zones 1 and 2.	Reduction of the toxicity, mobility, or volume associated with TCE contamination at the chemical plant area (Zones 1 and 2) would be accomplished.	The same as Alternative 8.

TABLE 14 (Cont.)

	Alternative 1: No Action	Alternative 2: Long-Term Monitoring	Alternative 3: Monitored Natural Attenuation	Alternative 4: Groundwater Removal and On-Site Treatment Using GAC and Ion Exchange	Alternative 7: Removal and On-Site Treatment of Groundwater (in Zones 1 and 2)	Alternative 8: In-Situ Treatment of TCE Using In-Well Vapor Stripping	Alternative 9: In-Situ Chemical Oxidation of TCE Using Fenton-Like Reagents
Short-term effectiveness	No potential impacts on workers or the environment because no activities would be undertaken.	Potential impacts are expected to be low, with less than one case of occupational injury and no occupational fatalities during proposed monitoring well construction. Any potential short-term environmental impacts would be limited to the immediate vicinity of the operable unit, and mitigative measures would be implemented to ensure minimal impacts to off-site areas.	The same as Alternative 2.	Potential impacts associated with construction of the extraction wells. Construction activities are estimated to result in up to 10 cases of occupational injury and less than one occupational fatality. Any potential short-term environmental impacts would be limited to the immediate vicinity of the operable unit, and mitigative measures would be applied to ensure minimal impacts to off-site areas.	Expected to be low, with less than nine cases of occupational injury and no occupational fatalities during operations and well construction activities. Any potential short-term environmental impacts would be limited to the immediate vicinity of the operable unit, and mitigative measures would be applied to ensure minimal impacts to off-site areas.	The same as Alternative 7.	The same as Alternative 7.
Implementability	No implementability concerns because no action would be taken nor would any future activities be considered.	Few implementability concerns because of the limited actions taken. Current monitoring operations would continue with the use of readily available resources.	The same as Alternative 2.	Uncertainties with implementation of this alternative are associated with the need for location (or area)-specific hydrogeologic data to verify the appropriateness of assumptions applied in the evaluations. Groundwater treatment technologies have been demonstrated at full-scale implementation for similar contaminants.	Uncertainties with implementation of this alternative are associated with specific hydrogeologic data that indicate dewatering and very slow recovery of the aquifer as observed from the recent pump test performed in the area of Zones 1 and 2.	Uncertainties with implementation of this alternative are relative to the generation of a vertical circulation pattern.	Implementability indicated by recent pump test performance; introduction of materials was possible.
Cost	Lowest future cost.	Annual monitoring costs are estimated to be $0.4 million.	Capital costs of approximately $0.3 million, primarily for construction of additional wells. The present-worth cost is estimated to range between $3 million and $4 million.	On the basis of an estimate of 24 extraction wells, capital costs are estimated to be approximately $7 million, with the 30-year present worth cost estimated to range between $15 million and $24 million. The least cost-effective of the seven alternatives because the degree of protectiveness provided is not commensurate with the significantly greater cost.	Capital costs are estimated to be approximately $4 million, with the 30-year present-worth cost estimated to range between $11 million and $16 million. Provides some increases in protection via mass reducation in Zones 1 and 2.	Capital cost estimated to range between $1 million and $3 million. Annual costs are estimated to be $0.4 million for monitoring.	The most cost-effective for management of TCE contamination as compared with Alternatives 7 and 8; capital cost estimated to be approximately $0.5 million and includes the material costs of the chemical reagents. Annual costs are estimated to be $0.4 million and are associated with groundwater monitoring. This alternative provides an increase in protectiveness via mass reduction of TCE that is proportionate to the cost.

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APPENDIX A:

TIME-DEPENDENT RESIDUAL CONTAMINANT CONCENTRATIONS

Cleanup times for the contaminants of concern (COCs) for the seven zones at the chemical plant area were calculated using the following expression:

$$\Delta t = \frac{R ln(\frac{C_0}{C_w}) L W t_h \phi}{NQ} . \tag{A.1}$$

Use of this equation assumes that the removal rate of a contaminant from a zone decreases exponentially with time. That is,

$$\frac{dC}{dt} = -\lambda C , \tag{A.2}$$

where λ is an effective decay constant for the process, and C is the residual concentration.

The solution to Equation A.2 is given by the relation:

$$C = C_0 e^{-\lambda t} , \tag{A.3}$$

where C_0 is the contaminant's initial concentration. The fraction of contaminant removed during time t is then derived by subtracting C/C_0 from 1.0.

The effective half-life for the process is given by

$$\Delta t_{1/2} = \ln(2) \frac{R L W t_h \phi}{NQ} . \tag{A.4}$$

By using Equation A.4, Equation A.3 can be rewritten as

$$C = C_0 e^{-\frac{NQt}{RLWt_h\phi}} . \qquad (A.5)$$

For a given zone, the residual contaminant concentration thus decreases exponentially with time and the number of pore volumes of the zone and is an inverse exponential function of the contaminant's retardation.

Figures A.1 through A.7 show the residual fraction of contamination remaining in each of the seven zones for each of the COCs. (Note that the actual contaminant concentrations can be obtained by multiplying the residual fraction times the initial concentrations). As expected, contaminants that have the largest retardation coefficients (e.g., uranium in Zone 1, Figure A.1) have the largest residual fractions as a function of time. Contaminants with the smallest retardation coefficients decrease the quickest and have the smallest residual fractions as a function of time (e.g., TCE in Zone 1, Figure A.1).

The above time-dependent behavior is very idealized and is subject to a large degree of uncertainty introduced by the actual arrangement of the extraction wells, the contaminant's spatial distribution, and heterogeneity in the aquifer. However, the method is useful for illustrating ideal system behavior.

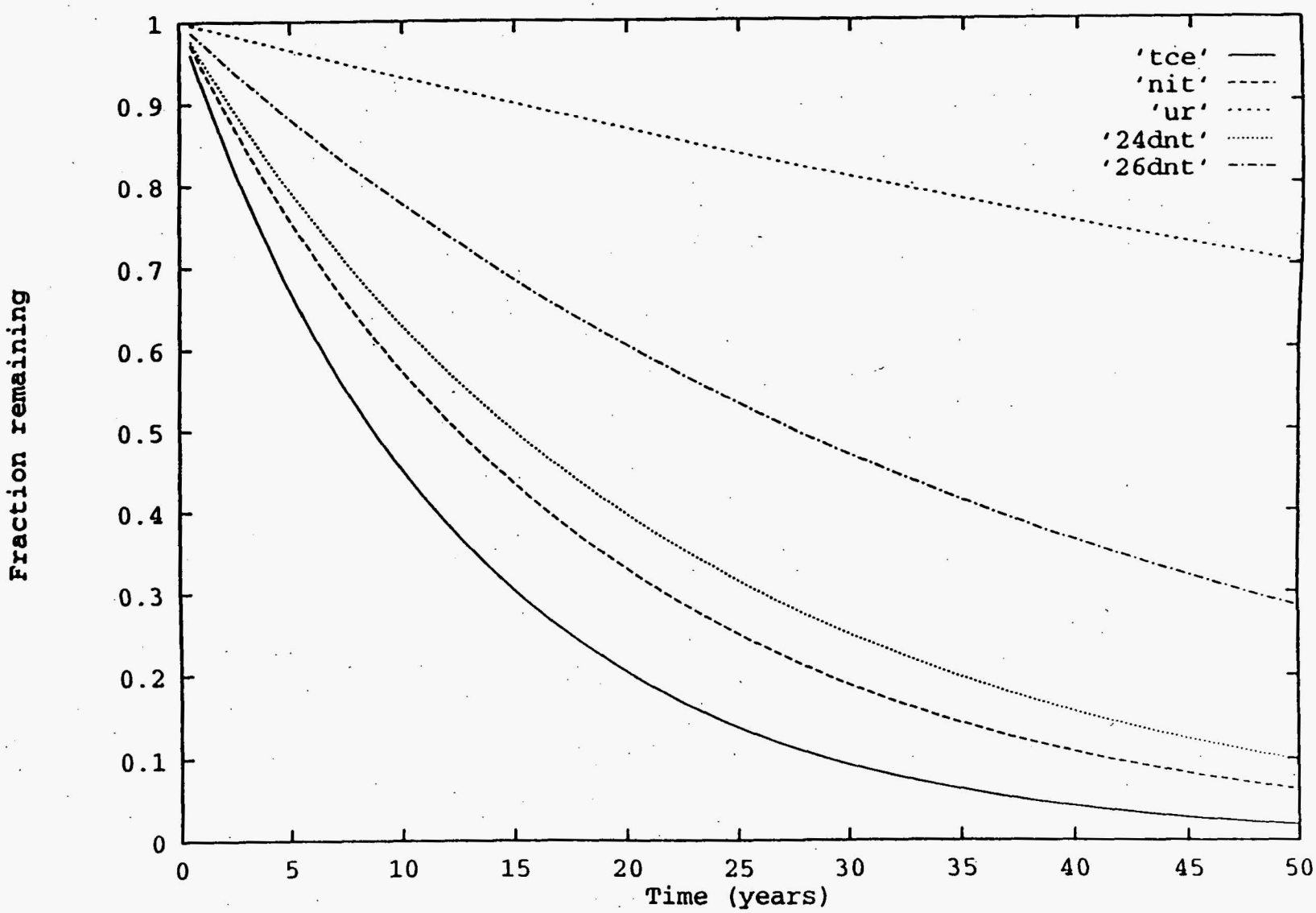

FIGURE A.1 Residual Contaminant Concentrations in Zone 1

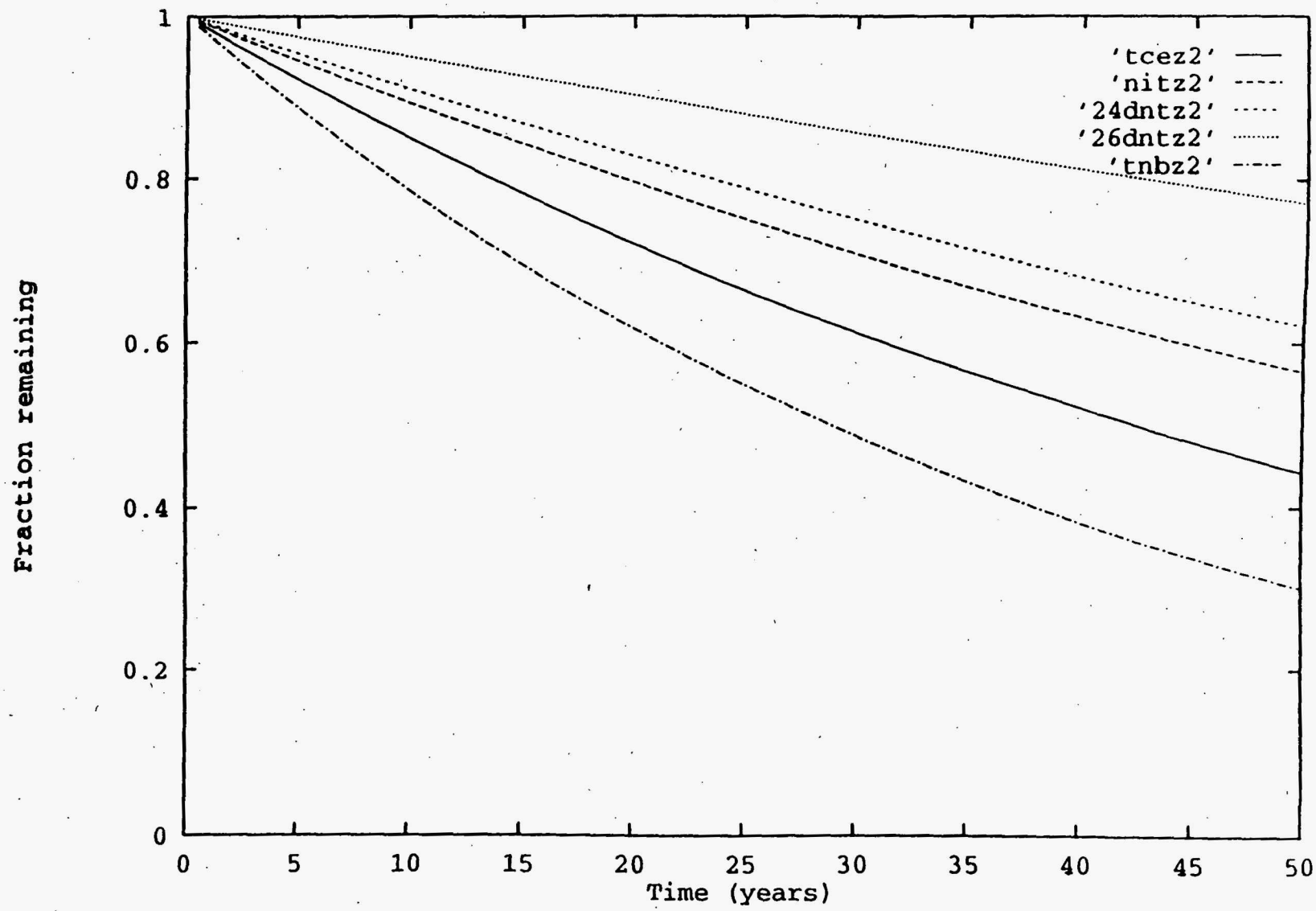

FIGURE A.2 Residual Contaminant Concentrations in Zone 2

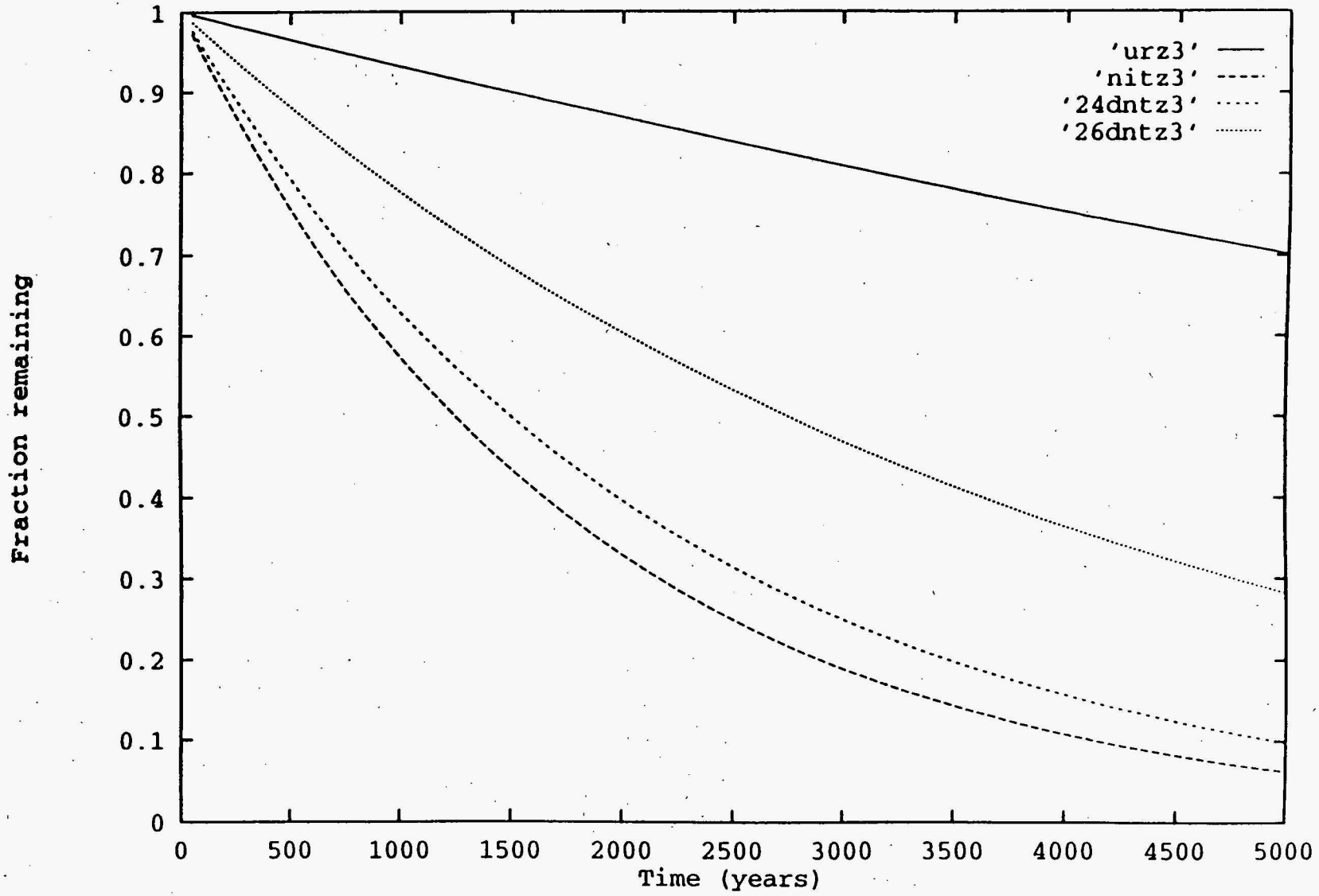

FIGURE A.3 Residual Contaminant Concentrations in Zone 3

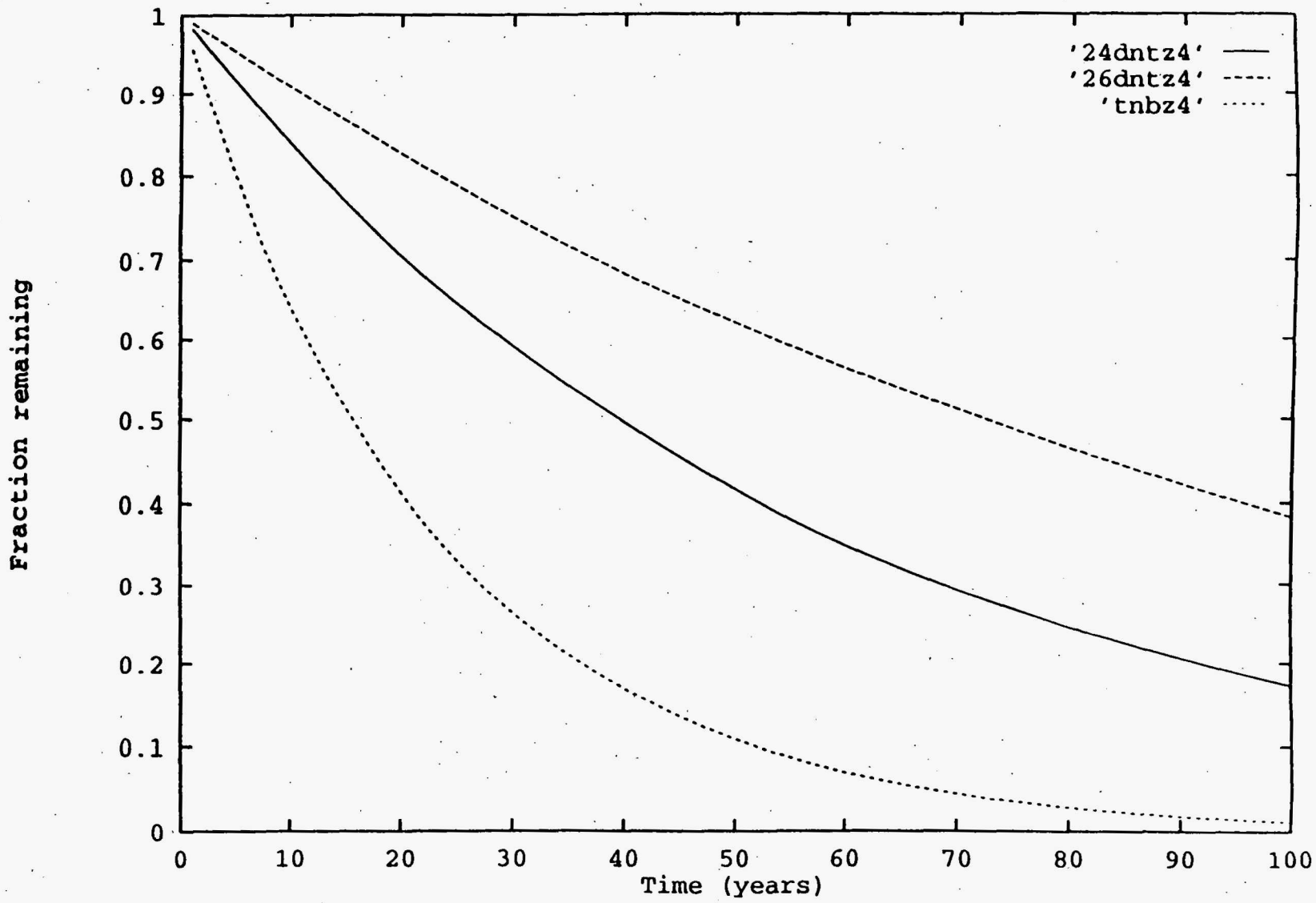

FIGURE A.4 Residual Contaminant Concentrations in Zone 4

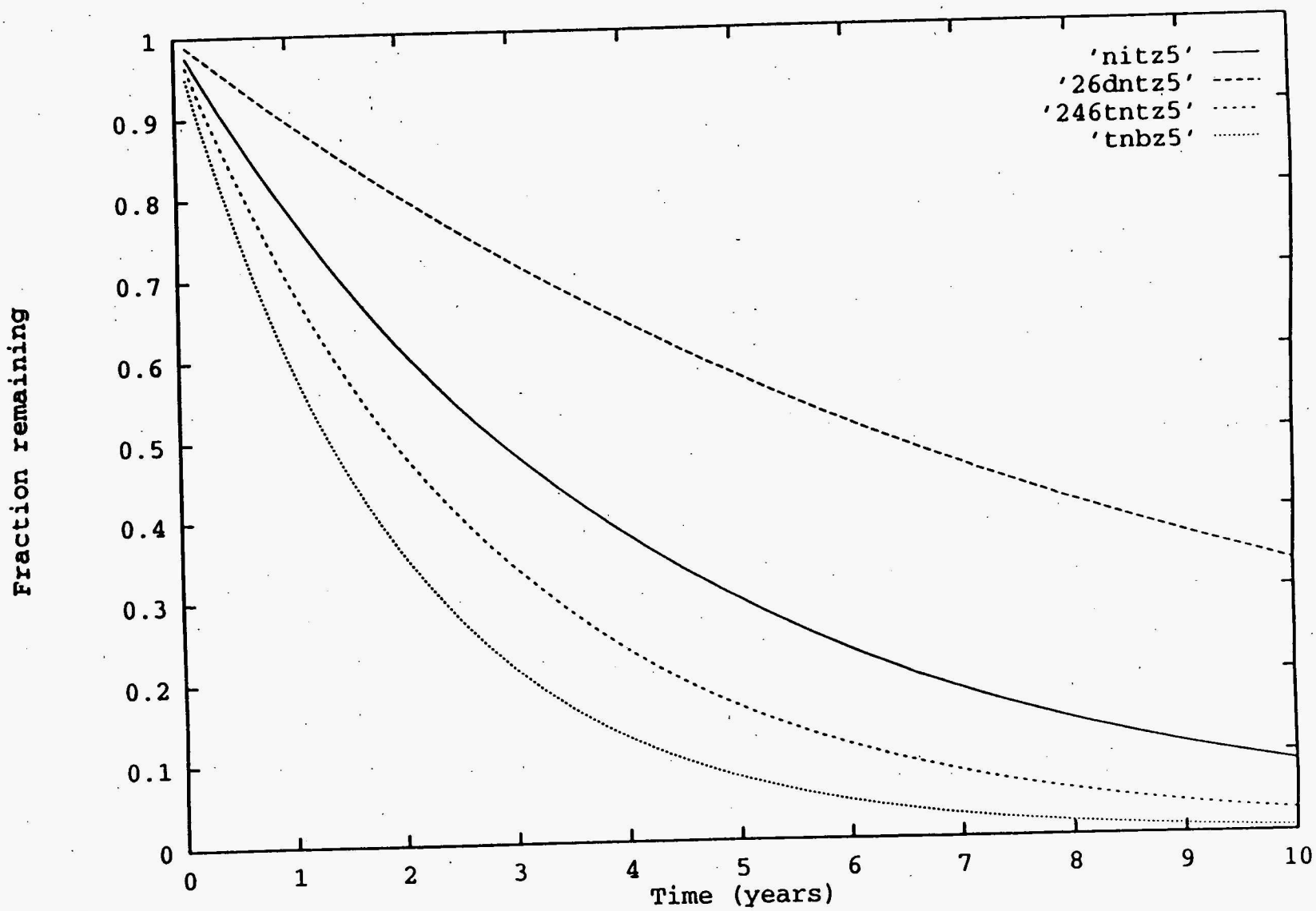

FIGURE A.5 Residual Contaminant Concentrations in Zone 5

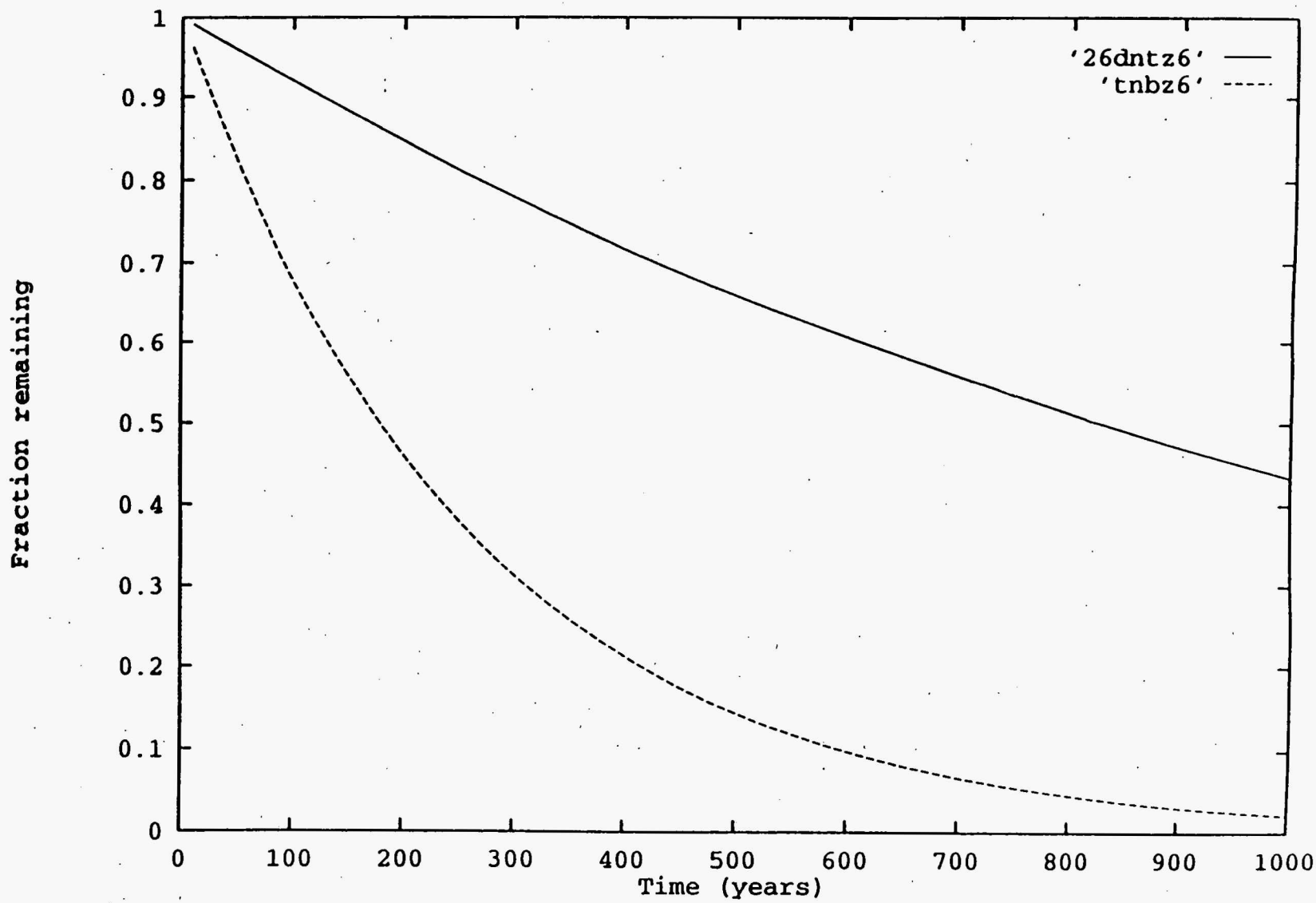

FIGURE A.6 Residual Contaminant Concentrations in Zone 6

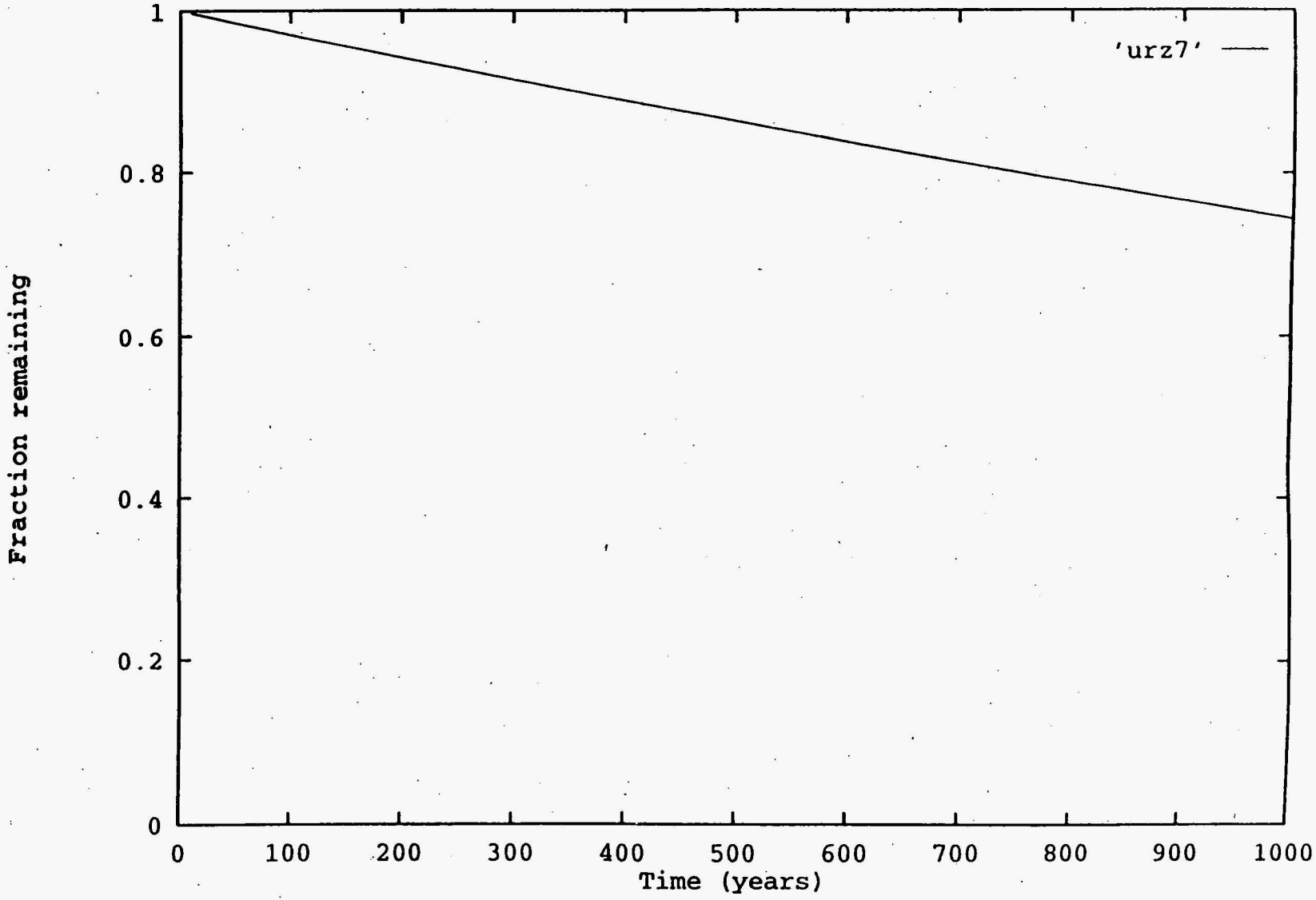

FIGURE A.7 Residual Contaminant Concentrations in Zone 7