Technical Memorandum on Natural Attenuation

Texarkana Wood Preserving Company Site
Texarkana, Bowie County, Texas

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LIST OF ACRONYMS AND ABBREVIATIONS

µg/L	Micrograms per Liter
^{13}C	carbon 13
bgs	Below Ground Surface
BTEX	Benzene, Toluene, Ethylbenzene, and Xylene
CLP	Contract Laboratory Program
cm/sec	Centimeters per second
COC	Contaminant of Concern
CP	Chlorophenol
DCP	Dichlorophenols
DHC	*Dehalococcoides*
DNAPL	Dense Non-Aqueous Phase Liquid
DO	Dissolved Oxygen
DSB	*Desulfitobacterium*
DWBZ	Deep Water Bearing Zone
EA	EA Engineering, Science, and Technology, Inc.
EPA	U.S. Environmental Protection Agency
ft/day	Feet per Day
ft/ft	Feet per Foot
GZ	Gravel Zone
IC	Institutional Control
Iron(II)	Ferrous Iron
Iron(III)	Ferric Iron
IWBZ	Intermediate Water Bearing Zone
mg/L	Milligram(s) per Liter
mL	Milliliter(s)
MNA	Monitored Natural Attenuation
mV	millivolt
ORP	Oxidation-Reduction Potential
OSWER	Office of Solid Waste and Emergency Response
PCP	Pentachlorophenol
PFLA	Phospholipid Fatty Acids
qPCR	Quantitative Polymerase Chain Reaction

Redox	Oxidation - Reduction
ROD	Record of Decision
SIP	Stable Isotope Probing
Site	Texarkana Wood Preserving Company Superfund Site
S/S	Solidification/Stabilization
SWBZ	Shallow Water Bearing Zone
TeCP	Tetrachlorophenol
TCP	Trichlorophenol
TOC	Total Organic Carbon

1. INTRODUCTION

This Technical Memorandum on Natural Attenuation for the Texarkana Wood Preserving Company Site (Site) located in Texarkana, Bowie County, Texas, has been prepared by EA Engineering, Science, and Technology, Inc. (EA) for the U.S. Environmental Protection Agency (EPA) Region 6 as part of Task Order No. 0058-RDRD-0691. The Technical Memorandum presents evidence for the occurrence of natural attenuation at the Site to show the efficacy of monitored natural attenuation (MNA) as part of a planned remedial action to stabilize or reduce the extent of impacted ground water between Site source areas and nearby Days Creek.

The contaminants of concern (COCs) at the Site are naphthalene and pentachlorophenol (PCP), which have caused impacts to ground water, surface soils, and subsurface soils. In the Record of Decision (ROD) for the Site, the major components of the selected remedy include:

- Excavation and consolidation of soil
- In-situ Solidification/Stabilization (S/S) of dense non-aqueous phase liquid (DNAPL) source material
- Long-term ground water monitoring
- Institutional controls (ICs) to prevent exposure to surface soil and ground water.

In the future, MNA may be added to the remedy, in an amendment to the ROD.

1.1 Objective

The purpose of this technical memorandum is to: (1) demonstrate that natural attenuation processes have occurred and are continuing at present and (2) evaluate the potential effectiveness of MNA to stabilize and/or reduce COC concentrations and the extent of the COC plume following implementation of the excavation and in-situ S/S stages of the remedial action.

EPA (1999) describes MNA as “reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods. The 'natural attenuation processes' that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. These in-situ processes include biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants."

The EPA Office of Solid Waste and Emergency Response (OSWER) Directive 9200.4-17P (EPA 1999) identifies three lines of evidence that can be used to estimate attenuation rates and remediation timeframe, including:

- Historical ground water and/or soil chemistry data that demonstrate a clear and meaningful trend of decreasing contaminant mass and/or concentration over time at appropriate monitoring or sampling points. (In the case of a ground water plume, decreasing concentrations should not be solely the result of plume migration.)

- Hydrogeologic and geochemical data that can be used to demonstrate indirectly the type(s) of natural attenuation processes active at the Site, and the rate at which such processes will reduce contaminant concentrations to required levels.

- Data from field or microcosm studies (conducted in or with actual contaminated site media) which directly demonstrate the occurrence of a particular natural attenuation process at the Site and its ability to degrade the contaminants of concern (typically used to demonstrate biological degradation processes only).

Data supporting these three lines of evidence have been collected and compiled, and will be evaluated within this technical memorandum.

1.2 Site Background Information

The Texarkana Site was used for lumber-related activities since the early 1900s, and wood preserving activities may have begun in the early 1950s. It is certain that by 1961, wood preserving operations using PCP and creosote were occurring on the southwestern portion of the Site. The wood-preserving operation consisted of a process building, a pressurized retort, process waste and treatment ponds, and preserved wood-drying areas. Two ponds were later added on the southeast side of Lubbock Street to serve as wastewater evaporation ponds.

In the latter part of 1971 or early 1972, creosoting operations were moved to improved facilities on the northwest portion of the Site. The improved facilities included improved wastewater treatment facilities, which were surrounded by concrete dikes designed to contain potential spillage and runoff. Following treatment, wastewater from creosote and PCP operations was released into a series of three evaporation ponds on the northeast part of the Site. The Texarkana Site ceased operations and closed in August 1984.

The principal soil and ground water contaminants at the Texarkana Site include polynuclear aromatic hydrocarbons and PCP that are associated with former wood-preserving activities. Although metals, and benzene, toluene, ethylbenzene, and xylenes (BTEX) were detected at the Texarkana Site, they were not considered principal COCs.

1.2.1 Site Description and Physical Setting

The Texarkana Site is located at 1001 Lubbock Street in Bowie County, Texas, just outside the city limits of Texarkana. It encompasses approximately 26 acres within a 100-year flood plain. The Site is bounded to the west by a railroad right-of-way and vacant land to the north, south, and east. Days Creek, a tributary of the Sulphur River, is located approximately 500 feet east of the Site, flowing to the south-southwest (Figure 1-1). Approximately 200 people reside within one-third mile of the Site. The nearest residence and businesses are located approximately one-

quarter mile to the west, beyond the railroad tracks. There are no schools in the immediate area and the nearest private drinking water well is approximately one-half mile to the east. The majority of drinking water in the area is supplied by Wright Patman Lake, located approximately 12 miles south of the Site.

1.2.2 Geology and Hydrogeology

The geology of the Site consists of Quaternary deposits that rest unconformably on the Tertiary Wilcox Formation. The Quaternary deposits appear to be upward fining fluvial deposits of Days Creek. The base of the Quaternary deposits consists of coarse sand and gravel that exhibits a sharp contact with the underlying Wilcox Formation, typical of channel deposits. The basal gravel is typically overlain by poorly to moderately sorted sand typical of transverse bars. Overlying the sand is sandy clay, silty fine sand, clayey silt, and silt clay, representing over-bank deposits. The Quaternary sequence is thin, typically 11 to 17 feet thick, and is non-repeating.

The Shallow Water Bearing Zone (SWBZ) consists of saturated soils within a gravel zone (GZ). Monitoring wells in the SWBZ (Figure 1-2) have completion depths to approximately 16 feet below ground surface (bgs). Depth to water ranges from 6 to 10 feet bgs, and the average GZ saturated thickness is 7 feet. In general, ground water flow is southeastward towards Days Creek (Figure 1-3). Hydraulic gradient is approximately 0.006 to 0.007 feet per foot (ft/ft). The average hydraulic conductivity value derived from pump tests is approximately 10 feet per day (ft/day) (Weston Solutions 2003) to 19 ft/day (EA 2008). Assuming an effective porosity of 0.3, seepage velocity is approximately 0.2 to 0.4 ft/day.

The Intermediate Water Bearing Zone (IWBZ) consists of several units separated from the GZ by thin, discontinuous clay laminations. The IWBZ extends to a depth of approximately 90 feet bgs. Monitoring wells in the IWBZ (Figure 1-2) have completion depths ranging from 56 to 63 feet bgs. The ground water flow direction of the IWBZ, like the SWBZ, is primarily towards the southeast. The hydraulic gradient has been determined to be 0.0017 ft/ft, and the hydraulic conductivity is approximately 1.2 ft/day (EA 2008).

Monitoring wells in the Deep Water Bearing Zone (DWBZ) (Figure 1-2) have completion depths to approximately 120 feet bgs. Hydraulic conductivity in the DWBZ is approximately 2.7 feet/day (EA 2008).

1.3 Analytical Approach

Subsequent sections of this report consider the biochemical mechanisms by which natural attenuation occurs, the results of data collection to assess the efficacy of those mechanisms, and conclusions that can be drawn from those results.

2. BIODEGRADATION MECHANISMS

This section describes the naphthalene and PCP biodegradation process, including aerobic and anaerobic pathways.

2.1 Biodegradation of Naphthalene

Effective aerobic and anaerobic pathways for biodegradation of naphthalene have been described and presented by various researchers as summarized below. The practical use of these pathways in MNA evaluations is somewhat limited, however, because chemical analyses that include naphthalene biodegradation products are not generally available within the EPA Contract Laboratory Program (CLP) or from commercial laboratories.

Aerobic biodegradation of naphthalene has been studied extensively and is thermodynamically favored over the anaerobic pathway. Naphthalene is initially oxidized, breaking the benzene double bonds with the help of dioxygenase to form cis-dihydrodiols (Bamforth and Singleton 2005). These dihydrodiols are dehydrogenated to form dihydroxylated intermediates, which can then be further metabolized via catechols to carbon dioxide and water (Bamforth and Singleton 2005).

There is a large diversity of bacteria that is responsible for oxidizing naphthalene using dioxygenase enzymes, including organisms from the genus *Pseudomonas* and *Rhodococcus* (Bamforth and Singleton, 2005). A few bacteria, such as *Mycobacterium sp*., are also able to oxidize naphthalene with the cytochrome P_{450} monoxygenase enzyme (Bamforth and Singleton 2005).

Bamforth and Singleton (2005) determined that the potential exists to degrade naphthalene in the absence of oxygen. The first step in anaerobic biodegradation of naphthalene is the carboxylation of the aromatic ring to 2-naphthoic acid, which may activate the aromatic prior to hydrolysis (Bamforth and Singleton, 2005). Stepwise reduction of 2-naphthoic acid via a series of hydrogenation reactions results in decaclin-2-carboxylic acid, which is subsequently converted to decahydro-2-naphthoic acid (Bamforth and Singleton, 2005). Ring fission and mineralization allow the decahydro-2-carboxylic acid to break down into carbon dioxide (Young and Phelps, 2005).

Zhang and Young (1997) showed that anaerobic degradation of naphthalene was possible under sulfate reducing conditions, and Al-Bashir et al. (1990) showed that it was possible under denitrifying conditions. Additionally, Al-Bashir et al. (1990) also proved that water saturated with naphthalene would allow for zero order (i.e, exponential) degradation with respect to naphthalene concentration. Mihelcic and Luthy (1988a, b) and Bregnard et al. (1996) reported degradation of naphthalene with nitrate as the electron acceptor. However, Langenhoff et al. (1996), conducted experiments in which naphthalene degradation was not observed under methanogenic or iron-reducing conditions. Additionally, these experiments showed only partial naphthalene degradation under manganese reducing conditions.

2.2 Biodegradation of Pentachlorophenol

Both aerobic and anaerobic conditions facilitate biodegradation of PCP with the presence of suitable bacteria. PCP provides a carbon source for microorganisms to carry out metabolic processes with the help of macro nutrients (nitrogen and phosphorus), micro nutrients (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, S^{2-}), co-factors such as heavy metals), and electron acceptors (Farhadian et al. 2008). Aerobic biodegradation is often limited by the amount of dissolved oxygen present, requiring engineered solutions such as air sparging or injection of oxygen-releasing compounds (Farhadian et al. 2008). However, anaerobic biodegradation generally is not limited by electron acceptor availability (Farhadian et al. 2008).

Highly halogenated aromatic compounds are difficult to biodegrade aerobically because chlorine substituents interfere with the action of dioxygenase enzymes that oxidatively cleave aromatic rings (Yu and Shepherd 1997). The initial removal of the halogens from the aromatic rings is essential to aerobic biodegradation (Yu and Shepherd 1997).

PCP can degrade aerobically to form tetrachloro-para-hydroquinone (Yu and Shepherd 1997). *Sphingomonas chlorophenolica* tend to dechlorinate the tetrachloro-para-hydroquinone to 6-chloro-1,2,4-tryhydroxybenzene (McCarthy et al. 1997) (Xun et al. 1992) (Xun and Orser, 1991). *Mycobacterium chlorophenolicum* tend to continue degradation of tetrachloro-para-hydroquinone with a second hydroxylation and subsequent reductive dechlorination (Häggblom et al. 1989) (Apajalahti and Salkinoja-Salonen, 1987a) (Apajalahti and Salkinoja-Salonen, 1987b). The end products of both aerobic degradation pathways are carbon dioxide and water (Yu and Shepherd, 1997).

Enzymes such as those found in bacteria from the *Desulfitobacterium* genus anaerobically biodegrade PCP to its less chlorinated phenolic derivatives (Tartakovsky et al. 1999). Under anaerobic conditions, it appears that PCP degrades to 2,3,4,5-tetrachlorophenol (2,3,4,5-TeCP) and 2,3,4,6-TeCP, followed by trichlorophenol (2,3,5-TCP), dichlorophenols (3,4-DCP and 3,5-DCP), chlorophenol (3-CP), and phenol (Davis et al. 1994). The non-chlorinated phenol breaks down to carbon dioxide and methane (Yu and Shepherd 1997).

Several studies have been done to research the effectiveness of biodegradation of PCP in ground water. A study conducted with ground water from a former wood treating facility in Dania, Florida, concluded that biodegradation of PCP occurs readily at concentrations of less than 20 milligrams per liter (mg/L) PCP, resulting in an increased concentration of daughter products (Davis et al. 1994). However, biodegration rates of PCP concentrations above 20 mg/L were substantially lower (Davis et al. 1994). This inhibited rate of biodegradation is attributed to the lack of bacterial ability to survive in waters with such high PCP concentrations. Specifically, the study mentions the limited growth of *Pseudomonas sp*. and *Arthrobacter sp*. in high PCP-concentration environments (Davis et al. 1994).

A more recent study conducted in Taiwan with aerobic *Sphingobium chlorophenolicum* (referred to as *Sphingomonas chlorophenolica* in the article) shows that PCP can be degraded when in concentrations of up to 400 mg/L (Yang and Lee, 2007). However, degradation of PCP in

concentrations of 600 mg/L was not successful (Yang and Lee, 2007). In addition to examining the concentration limits for PCP biodegradation, this study also addressed factors such as the effect of inducing the *S. chlorophenolicum* cells with PCP and the effect of the presence of chloride on biodegradation of PCP. It was concluded that pre-incubating the *S. chlorophenolicum* cells with PCP in order to induce PCP degrading enzymes almost doubled the rate of PCP degradation when compared to cells that were not pre-incubated with PCP (Yang and Lee, 2007). PCP removal efficiency during experiments for this study was not influenced by the presence of various concentrations of chloride (Yang and Lee, 2007).

3. SITE-SPECIFIC LINES OF EVIDENCE

The focus of this document is to assess the potential for MNA to be viable at the Site for use in tandem with other remedial components such as S/S. However, the analysis was done prior to conducting S/S activities, and therefore it does not assume that other technologies have been previously applied. This evaluation uses site-specific data in the three-tiered weight of evidence approach put forth by EPA (1999). A summary of this approach, as applied herein, is provided in Table 3-1.

3.1 Contaminant Distribution, Trend Analysis, and Degradation Products

Prior to the 2010 ground water sampling, it was expected that nearly all of the ground water contamination, including the greatest distribution and highest concentrations, would be found in the SWBZ (EA 2007a; EA 2008). This was confirmed in the August 2010 sampling event. Results of the 2010 ground water and surface water sampling are provided in Table 3-2 and summarized below, along with an analysis of historical COC concentration trends and modeling of 2010 COC concentrations along the centerline of an historical plume.

3.1.1 Distribution of Contaminants of Concern

Figures 3-1 and 3-2 present the naphthalene distribution for samples collected from monitoring wells that are finished in the SWBZ and IWBZ, respectively, during the October 2003, November 2007, and August 2010 sampling events. A comparison of the three sampling events indicates that naphthalene concentrations have declined substantially in MW-36, MW-33, and MW-02, which are located in the center of the dissolved phase plume. Naphthalene was detected in newly installed downgradient wells SRD-3 at 517 micrograms per liter (µg/L) and SRD-4 at 2,230 µg/L (Table 3-2). Naphthalene concentrations in the perimeter monitoring wells (MW-03, MW-06, MW-08, MW-09, and SRD-9) were below detection limits during the August 2010 sampling event (Table 3-2).

A semi-quantitative assessment of the extent of the naphthalene plume appears to indicate that biodegradation is actively controlling contaminant transport. Given the age of the continuous DNAPL sources (creosoting operations were conducted from about 1954 to 1984) and a seepage velocity of 0.2 to 0.4 ft/day as discussed earlier, the edge of the plume within the SWBZ could theoretically extend more than 2,000 feet beyond the sources if there were no degradation. Because Days Creek is less than 2,000 feet from the contaminant sources, this result implies that there would be active contaminant discharge to the creek. Assuming no significant dilution by surface water in Days Creek, there currently is no evidence of such discharge because there were no detections in the surface water of naphthalene, PCP, or products of PCP degradation (Table 3-2). In addition, ground water results indicate that the edge of the plume is fully delineated and that it does not extend to Days Creek (Figure 3-1). This provides evidence that biodegradation is controlling the extent of the dissolved phase SWBZ plume.

Naphthalene was not detected in the IWBZ with the exception of monitoring well IRD-1 at a concentration of 3.2 µg/L. This detection could be the result of residual contamination during

monitoring well construction in 2010. Similar naphthalene detections were present in MW-31 and MW-18 following well installation in 2003. Naphthalene was not detected in MW-31 or MW-18 during subsequent sampling events. IRD-1 will be sampled during the next routine sampling event to determine if naphthalene is present.

Figures 3-3 and 3-4 present the PCP distribution for samples collected from monitoring wells in the SWBZ and IWBZ, respectively, during the October 2003, November 2007, and August 2010 sampling events. A comparison of the three sampling events indicates that the PCP concentrations have declined considerably. Monitoring wells MW-36, MW-33, and MW-02 contained PCP at concentrations of 3,580 µg/L, 4,850 µg/L, and 463 µg/L, respectively, during the 2003 sampling event, but PCP was not detected in these monitoring wells in August 2010. PCP concentrations in the perimeter monitoring wells have remained below detection limits. PCP was not detected in the IWBZ. PCP and its daughter products also were not detected in the surface water of Days Creek.

3.1.2 Historical Concentration Trend Analysis

Historical concentrations of naphthalene and PCP dating back to 2003 were compiled and analyzed to determine if meaningful trends existed to demonstrate stable or decreasing concentrations over time. Concentrations of naphthalene and/or PCP for wells that included detections substantially above the detection limit were plotted in time series to illustrate potential trends. These plots are provided in Figures 3-5 through 3-16.
Natural attenuation rates were modeled based on the following exponential function:

where:

C_t = pollutant concentration at monitoring year t,
C_o = pollutant concentration at monitoring year t=0,
k_d = natural attenuation rate ($year^{-1}$), and
t = time (years).

The C_o and k_d parameters were fitted from the data using time series of naphthalene and PCP concentrations in each of the 12 monitoring wells. Typically, pollutant concentrations followed a rise and fall pattern, and only the falling limb was included in the model to assess natural attenuation. Non-detects were set to one half of the detection limit. The fitted natural attenuation rates for naphthalene and PCP are provided in Tables 3-3 and 3-4, respectively. Based on these analyses, the calculated half-lives for naphthalene range from 0.7 to 2.13 years (Table 3-3); for PCP, the calculated half-lives range from 0.70 to 1.28 years (Table 3-4).

3.1.3 Presence of Degradation Products

PCP degradation products 2,4,5-TCP and 2,4-DCP have been observed in monitoring wells MW-02, MW-05, MW-33, MW-35, and MW-36, which are located within the PCP plume. The 2,4,5-TCP and 2,4-DCP concentrations are summarized in Table 3-2. The data indicate that 2,4,5-TCP was present in more wells than 2,4-DCP, which is consistent with the PCP biodegradation sequence. These compounds were detected in only a few monitoring wells, and the concentrations are small when compared to the amount of PCP detected. Therefore, it appears these compounds are not associated with the source but are degradation products of PCP. The low concentrations of degradation products could be a result of differing degradation rates or the multiple additional degradation products that are not analyzed routinely in CLP or commercial laboratories.

3.1.4 Biodegradation Modeling

The EPA model BIOSCREEN (EPA 1996) was used to examine whether downgradient concentrations along a plume centerline were best explained with or without first-order decay, based on approximate flow and transport parameters from site data and/or appropriate default model values. The simulation was based on the naphthalene plume emanating from the southwestern part of the site (Figure 3-17) that was described as the "Old Process Area", which operated from approximately 1954 to 1974 (Arnett 1999). This area was chosen primarily because there was only one identified contaminant source and a relatively long, linear plume, which closely fits the BIOSCREEN model constraints.

BIOSCREEN input parameters are shown in Table 3-5. The simulation was run using the average biodegradation parameters for naphthalene calculated from historical Site data during the temporal trend analyses. Two simulation types (with and without biodegradation) were run in BIOSCREEN to determine which attained the best fit when compared to field concentrations.

Figure 3-18 shows the output from the BIOSCREEN simulations for naphthalene using no biodegradation and using the average first-order decay rate from the temporal trends. Based on the output, it is clear that use of a degradation factor provides a better fit to the Site data than no degradation. The model results also imply that the average temporal degradation rate may be too conservative to match the data on a spatial scale. This could be because of scale issues (i.e., different factors may be acting over space vs. over time) or because the BIOSCREEN input parameters are too general or inaccurate, or because site characteristics are more complex than BIOSCREEN is capable of simulating. In general, the simulation is sensitive to the degradation reaction rate and hydraulic conductivity value. Arnett (1999) and Weston Solutions (2003) reported average hydraulic conductivity values of about 1 ft/day (3.5E-4 centimeters per second [cm/sec]) and 10 ft/day (3.5E-3 cm/sec), respectively, each of which is lower than the hydraulic conductivity used in the model presented here (19 ft/day [6.7E-3 cm/sec]). Use of either of these simulated hydraulic conductivity values results in a better fit to the 2010 concentration data, and a faster degradation rate also provides a better fit. Regardless, BIOSCREEN simulation results are consistent with significant biodegradation of COCs and do not support the premise that biodegradation is minimal or nonexistent at the Site.

3.2 Geochemical Analysis

The purpose of the geochemical analysis is to evaluate the distribution of ground water indicators and determine if evidence exists that biodegradation processes are occurring at the Site. Oxidation-reduction (Redox) indicators such as oxidation-reduction potential (ORP), concentrations of dissolved oxygen, nitrate, ferrous iron, sulfate, and methane can be indicative of the type and degree of biodegradation that has occurred and is occurring. Certain field parameters commonly measured during ground water sampling (i.e., pH, total organic carbon [TOC], and water temperature) can show whether conditions are favorable for microbial population growth. Additionally, alkalinity and chloride concentrations within or downgradient of a contaminant plume can be compared with background concentrations to determine if mineralization of organic compounds has occurred, resulting in a buildup of these parameters. A summary of the geochemical analysis is included in Table 3-6.

3.2.1 Oxidation-Reduction (Redox) Indicators

ORP—The ORP of ground water is a measure of electron activity and is an indicator of the relative tendency of a solution to accept or transfer electrons. Oxidation-reduction reactions in ground water containing organic compounds (natural or anthropogenic) usually are biologically mediated, and therefore the ORP of a ground water system depends upon and influences rates of biodegradation. Knowledge of the ORP of ground water is also important because some biological processes operate only within a prescribed range of ORP conditions. ORP measurements can be used to provide real-time data on the location of the contaminant plume, especially in areas undergoing anaerobic biodegradation. Three ranges of ORP are applicable in determining the likelihood of anaerobic biodegradation:

- < -100 millivolts (mV) indicates “reductive pathway likely”
  (MW-28, SRD-4, SRD-6, SRD-7, and SRD-8)
- < 50 mV indicates “reductive pathway possible”
  (MW-33, SRD-1, SRD-2, SRD-3, and SRD-5)
- >+50 mV indicates “reductive pathway unlikely”
  (MW-13 and MW-23).

At the Site, the lowest ORP measurements (indicating more reducing conditions) are located in wells such as SRD-8 (-191 mV), and MW-28 (-175 mV) (Table 3-6) on the downgradient portion of the naphthalene plume and beyond the downgradient portion of the PCP plume (Figure 3-1). The highest ORP measurements (indicating more oxidizing conditions) are located outside of the plume area in up gradient well MW-23 (110 mV) and in well MW-13 (94 mV) (Table 3-6), located just outside of the naphthalene plume area (Figure 3-1).

Dissolved Oxygen (DO)—Dissolved oxygen is the most thermodynamically favored electron acceptor used by microbes for the biodegradation of organic carbon (EPA 1998). As a result,

DO frequently gets utilized and depleted quickly in the biodegradation process, resulting in anaerobic conditions. DO concentrations less than about 0.5 mg/L usually indicate anaerobic conditions. Wells MW-28 (1.13 mg/L), SRD-2 (1.91 mg/L), SRD-3 (0.9 mg/L), SRD-5 (1.99 mg/L), and SRD-8 (2.6 mg/L) each had DO concentrations above 0.5 mg/L (Table 3-6). The DO and ORP parameters did not always agree. The lowest (most anaerobic) ORP values were in wells MW-28 and SRD-5, each of which had over 1 mg/L DO. Wells MW-13 and MW-23, which had positive (aerobic) ORP values and are located outside the plume (Figure 3-1), had DO concentrations less than 0.5 mg/L (indicating anaerobic conditions).

Nitrate—After DO is depleted in the microbiological treatment zone, nitrate and nitrite may be used as electron acceptors for anaerobic biodegradation of organic carbon via denitrification. In order for reductive dechlorination to occur, nitrate concentrations in the contaminated portion of the aquifer must be less than 1.0 mg/L. Nitrate levels were below 1.0 mg/L in all monitoring wells analyzed for MNA parameters (Table 3-6).

Ferrous Iron [Iron(II)]—Ferric iron (iron[III]) can be used as an electron acceptor during anaerobic biodegradation; iron(III) is reduced to iron(II). Therefore, iron(II) concentrations are an indicator of reducing conditions. Iron(II) concentrations above the threshold value of 1 mg/L were observed inside the plume in samples from wells MW-28, MW-33, SRD-1, SRD-2, SRD-5, SRD-6, and SRD-7; concentrations below 1 mg/L were observed outside the plume in samples from wells MW-13 and MW-23 (Table 3-6).

Sulfate—Sulfate may be used as an electron acceptor once DO and nitrate have been depleted. This process is known as sulfate reduction, and results in the production of sulfide. Sulfate concentrations exceeding 20 mg/L may compete with the reductive pathway. Sulfate concentrations less than 20 mg/L were observed inside the plume and on the leading edge of the naphthalene plume in wells MW-28 (11.9 mg/L) and SRD-7 (2.12 mg/L). Sulfate concentrations exceeding 20 mg/L were found outside of the plume in wells MW-13 (35.8 mg/L) and MW-23 (41.6 mg/L). The highest sulfate concentration was recorded in MW-33; this well has a history of high contaminant concentrations but did not contain naphthalene or PCP during the most recent sampling event (Figures 3-1 and 3-3).

Methane—During methanogenesis, acetate is either split to form carbon dioxide and methane, or carbon dioxide is used as an electron acceptor and then reduced to methane. Methanogenesis generally occurs after oxygen, nitrate, and sulfate have been depleted in the treatment zone. The presence of methane in ground water is indicative of strongly reducing conditions. Methane concentrations exceeded 0.5 mg/L in monitoring wells MW-33, SRD-1, SRD-2, SRD-5, and SRD-6, which are located inside the plume (Figures 3-1 and 3-3). The lowest methane concentrations were observed outside the plume (MW-13 and MW-23).

As mentioned above, it should be noted that the geochemical indicators (i.e., DO, ORP, nitrate, etc.) did not always definitively exhibit characteristics consistent with one reaction type (e.g., nitrate reduction or methanogenesis). This occurrence is relatively common; a potential reason for this is discussed in the BIOSCREEN user's manual (EPA 1996):

Alternative biochemical mechanisms exhibiting very similar energy potentials (e.g., aerobic oxidation and nitrate reduction) may occur concurrently when the preferred electron acceptor is reduced in concentration rather than fully depleted. Facultative aerobes, for example, can shift from aerobic metabolism to nitrate reduction when oxygen is present in low concentrations. Similarly, sulfate reduction and methanogenic reactions may occur together.

Another potential reason is that differing terminal electron acceptor conditions may exist in closely spaced microenvironments affected by ground water replenishment and other factors. Because naphthalene degrades best in aerobic conditions and PCP in anaerobic conditions, this type of environment would be favorable for degradation of both COCs.

3.2.2 Field Parameters

Field parameters such as pH, TOC, and temperature can indicate whether conditions are more or less favorable to biodegradation as these conditions affect survivability and growth of microorganisms. In general, pH of ground water at the Site is within the favorable range of 5 to 9 pH units; TOC is somewhat less than favorable as an available carbon source for reductive reactions; and relatively warm ground water temperature (exceeding 20°C) is favorable for microbial population growth, which would stimulate biodegradation.

3.2.3 Alkalinity and Chloride

The presence of alkalinity and/or chloride within or downgradient of a plume at concentrations substantially above (e.g., twice) background can be an indicator of complete mineralization of hydrocarbons. Complete mineralization of hydrocarbons (e.g., naphthalene) results in the creation of inorganic carbon dioxide and water, resulting in increased alkalinity. Mineralization of chlorinated hydrocarbons (e.g., PCP) results in the creation of inorganic carbon dioxide, water, and chloride ion, resulting in increased alkalinity and potentially higher downgradient concentrations of chloride.

Background concentrations of alkalinity and chloride were based on the 2010 concentrations from well MW-23, which is located up gradient from any known DNAPL source. Results from ground water sampling at the Site showed alkalinity at more than twice the background concentration in each well except for MW-13 and MW-28 (Table 3-6), which are located distant from any sources. The only ground water sample that had chloride concentrations more than twice the background level was SRD-1 (Table 3-6), located adjacent to a DNAPL source (Figures 3-1 and 3-3).

It is likely that the alkalinity in the downgradient wells is a result of CO_2 enrichment from the degradation and mineralization of naphthalene and possibly PCP. Naphthalene is and was more widespread in Site ground water than PCP. If the increased alkalinity were primarily related to PCP degradation, it is likely that chloride would be enriched in more wells than is apparent from the 2010 sampling. The absence of chloride enrichment, however, does not negate the other

positive evidence related to PCP degradation, as other mechanisms such as dilution or the smaller PCP source areas may have affected chloride concentrations in ground water.

3.3 Microbial Analysis

Microbial analyses conducted for this study included quantitative polymerase chain reaction (qPCR) and Stable Isotope Probing (SIP). Both analyses were conducted by Microbial Insights; the results are summarized below.

3.3.1 Quantitative Polymerase Chain Reaction (qPCR)

The qPCR analysis called CENSUS was used to test for the presence of dechlorinating bacteria, including the *Dehalococcoides* (DHC) and *Desulfitobacterium* (DSB) microbes, and for functional genes that are not specific with regard to microorganisms but are important with regard to regulating biodegradation of naphthalene and PCP along various aerobic pathways. The qPCR operates by replicating target gene sequences within a sample and using the replication speed and final gene concentration to extrapolate the organism or functional gene concentration in the original sample.

Based on the Site COCs, Microbial Insights recommended the following targets for CENSUS qPCR analyses:

- *Dehalococcoides* (reductive dechlorination of PCP possible by some species)
- *Desulfitobacterium* (reductive dechlorination of PCP possible by some species)
- PCP Regulator Gene (aerobic degradation of PCP)
- Maleylacetate Reductase (aerobic degradation of 2,4,6-TCP, which can be a degradation product of PCP)
- PCP-4-Monooxygenase (initiates aerobic degradation of PCP)
- Naphthalene Dioxygenase (aerobic degradation of naphthalene).

EA collected ground water samples from 12 monitoring wells in August 2010 and submitted the samples to Microbial Insights for qPCR analysis of the recommended targets. Results were interpreted using the following general concentration guidelines to categorize them for discussion purposes:

- Very Low – $< 1.0 \times 10^2$ cells/milliliter (mL)
- Low – $< 1.0 \times 10^3$ cells/mL
- Moderate – 1.0×10^4 to 1.0×10^5 cells/mL
- High – $> 1.0 \times 10^6$ cells/mL.

The guidelines are not definitive by themselves, but need to be interpreted in context with the chemicals present, degradation rates, daughter products, and redox reactions that are known or inferred from sampling data. The results of the qPCR analyses for each of the targets are provided in Table 3-6 and are summarized below.

Dehalococcoides—Under anaerobic conditions, PCP can serve as an electron acceptor for certain species of *Dehalococcoides*, resulting in partial dechlorination and the production of dichloro- and monochlorophenols (Microbial Insights 2009). At the Texarkana Site, *Dehalococcoides* was either present at very low levels or was not detected at the Site (Table 3-6), which likely indicates that it did not have a substantial affect on PCP degradation.

Desulfitobacterium—As with *Dehalococcoides*, PCP can serve as an electron acceptor for *Desulfitobacterium* (Microbial Insights 2009). *Desulfitobacterium* was present at moderate or high levels in each of the natural attenuation samples except for SRD-8 (Table 3-6), where PCP was not detected. Anaerobic PCP degradation products were detected in several wells, which is consistent with the presence of *Desulfitobacterium*.

PCP Regulator Gene—This is a functional gene that relates to aerobic degradation of PCP. Moderate levels of this gene were present in samples from wells MW-33, SRD-2, SRD-5, and SRD-6. Well SRD-2 was the only one of these four in which PCP was detected (Table 3-2).

Maleylacetate Reductase—This reductase gene is important in aerobic degradation of 2,4,6-TCP, which can be a degradation product of PCP. This gene was present at very low to low/moderate levels in ground water samples from the wells listed in Table 3-6. No 2,4,6-TCP was reported above the detection limit in the 2010 ground-water samples (Table 3-2).

PCP-4-Monooxygenase—This assay specifically targets oxygenase genes encoding the enzymes responsible for initial oxidation of PCP and aromatic ring cleavage (Microbial Insights 2009). This gene also was present at very low to low/moderate levels in ground water samples from the wells listed in Table 3-6.

Naphthalene Dioxygenase—This is important for the initial oxidation of naphthalene in aerobic naphthalene degradation (Bamforth and Singleton 2005) and was found at high levels in the samples from each of the wells listed in Table 3.6. Naphthalene degradation appears to be occurring at a relatively high rate at the Site, and it is likely that aerobic biodegradation, which is initiated by dioxygenase, is the dominant pathway for naphthalene attenuation in ground water at the Site.

In summary, the qPCR analyses indicated that sulfate-reducing bacteria capable of degrading PCP and that microorganisms that are capable of aerobic degradation of naphthalene were present onsite in numbers that suggest a good likelihood of effective biodegradation of the COCs through these pathways.

3.3.2 Stable Isotope Probing (SIP)

EA and Microbial Insights, Inc., conducted a SIP study for this MNA evaluation to determine if biodegradation of the contaminants of concern is occurring at the Site. The SIP method requires a bio-trap sampler baited with a synthesized form of the contaminants labeled with carbon 13 (^{13}C). Since ^{13}C occurs at a constant, low concentration in the environment, the labeled bait can be differentiated from the contaminants present at the Site. The existing microbial population acts on the labeled bait the same as it does on the site contaminants, so the quantitative results that can be obtained from the amendment are a reflection of the degradation processes that occur under ambient site conditions.

With the SIP method, biodegradation can be conclusively demonstrated as follows:

- The percent loss of the ^{13}C-labeled compounds provides an estimate of the degradation rates;
- Quantification of ^{13}C-enriched phospholipid fatty acids (PLFA) indicates incorporation into microbial biomass; and
- Quantification of ^{13}C-enriched dissolved inorganic carbon indicates contaminant mineralization.

On 11 August 2010, two bio-trap samplers were deployed in each of three monitoring wells (MW-33, SRD-2, and SRD-5). One of the samplers in each well was baited with ^{13}C labeled PCP; the second sampler was baited with ^{13}C labeled naphthalene. EA retrieved the samplers from the monitoring wells on 7 October 2010 and sent the samplers to Microbial Insights, Inc. for analysis. The results are summarized below.

Contaminant Loss—Microbial Insights was unable to determine pre- or post-deployment PCP concentrations on the bio-trap beads due to matrix interferences. For naphthalene, however, the comparison of pre-deployment and post-deployment concentrations in the samplers indicated a 51 percent loss in well MW-33, a 14 percent loss in well SRD-2, and a 26 percent loss in well SRD-5 during the 51 days that the samplers were deployed.

Biomass Concentrations—For wells MW-33, SRD-2, and SRD-5 (each of the wells analyzed this way), overall biomass concentrations were moderate, and enriched biomass was detected for both the naphthalene and PCP amended bio-traps, which indicates biological degradation of both compounds.

Dissolved Inorganic Carbon (DIC)—Quantification of DIC indicated utilization of naphthalene and PCP compounds in water from well MW-33, although naphthalene was utilized at a higher level than PCP. Both compounds exhibited a high level of mineralization in the SRD-2 samplers. In the SRD-5 samplers, a high level of naphthalene mineralization was indicated; PCP mineralization also occurred, but at a lower level than naphthalene.

In summary, the following results from the SIP method conclusively demonstrated COC biodegradation:

- Reduced naphthalene concentrations between the beginning and the end of deployment (note that PCP concentrations could not be determined due to matrix interferences, so concentration reduction could not be calculated);
- Biomass enriched with 13C labeled naphthalene and PCP; and,
- DIC enriched with labeled naphthalene and PCP.

In addition to this, the SIP method provided insight to the types of microbes responsible for biodegradation at the Site through PFLA analysis. The most abundant microorganisms were Proteobacteria, which are described as typically fast growing, utilizing many carbon sources, and adapting quickly to a variety of environments. Proteobacteria comprise one of the largest groups of bacteria, representing a wide variety of anaerobes and aerobes. This microbial population is consistent with the COCs on site (which degrade through anaerobic and aerobic pathways) and with the variety of electron acceptors at the site as described above.

4. CONCLUSIONS

The three lines of evidence put forth by EPA for demonstrating natural attenuation were evaluated at the Texarkana Wood Products Superfund Site to determine if MNA could be a viable component of Site remediation. Results of the evaluation are presented in Table 3-1 and they included the following:

Distribution of Contaminants of Concern indicates plume stability and/or reduction from 2003 to 2010. Monitoring wells located just exterior to the plume did not exhibit any COC detections. Several monitoring wells on the interior of the plume exhibited reduced concentrations from 2003 to 2010.

Historical Trend Analysis conclusively demonstrated significant downward concentration trends in several monitoring wells that had sufficiently long records of naphthalene and/or PCP detections.

Degradation Products from anaerobic PCP biodegradation pathways were present in several wells. Naphthalene degradation products are not commonly analyzed by CLP or commercial laboratories, and as a result were not found onsite.

Analytical Modeling using BIOSCREEN demonstrated that naphthalene concentrations along the centerline of a plume were more closely matched when a first-order decay component was included in the model as opposed to advective transport and hydrodynamic dispersion alone.

Geochemical Data indicate that redox conditions within the plume near source areas are more reduced than those at the edges or exterior to the plume. This indicates that electron acceptors are depleted within the plume due to biodegradation, and more oxidized conditions return after COCs are depleted.

Quantitative PCR demonstrated the presence of moderate to high levels of microbes and/or functional genes capable of degrading naphthalene and PCP.

SIP Analysis conclusively demonstrated naphthalene biodegradation through concentration reductions and demonstrated that biomass and dissolved inorganic carbon was enriched by naphthalene and PCP degradation.

Based on these lines of evidence, natural attenuation of naphthalene and PCP was clearly demonstrated to have occurred in the past and it is still occurring. It is therefore concluded that MNA will be a viable component to the overall remedial strategy at the Site.

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TABLES

TABLE 3-1. SITE-SPECIFIC LINES OF EVIDENCE SUPPORTING NATURAL ATTENUATION AS A COMPONENT OF THE REMEDIAL ACTION

Tier	Line of Evidence	Observed Behavior	Indicative of Effective NA?	Affirmed by Site Data?
1	Stable COC concentrations in downgradient and sentinel wells	Leading edge of plume appears stable based on sampling results from 2003, 2007, and 2010.	Yes	Yes
1	Historical ground water data that demonstrate a clear and meaningful trend of decreasing concentration over time at appropriate monitoring points	Time series data show concentration reduction or stability in individual wells with historical COC detections as far back as 1988. Anaerobic PCP degradation products present in several wells.	Yes	Yes
1	Analytical modeling indicates that biodegradation is controlling plume migration	BIOSCREEN model indicates that simulations including first-order decay provide a substantially better match to COC concentrations in groundwater along a plume centerline than simulations without a decay component.	Yes	Yes
2	Geochemical data indicate that conditions are more reduced near source areas than at or beyond the limits of the plume	MNA parameters collected during 2010 sampling are consistent with this line of evidence.	Yes	Yes
3	Direct microbial evidence of biodegradation of naphthalene and PCP	Results from SIP investigation showed naphthalene concentration reductions and enriched biomass in biotraps baited with ^{13}C labeled naphthalene and PCP.	Yes	Yes
3	Presence of microbes capable of degrading COCs	High concentrations of *Desulfitobacterium* present which are capable of anaerobically degrading PCP; high levels of Naphthalene dioxygenase enzyme, indicating capability of aerobic naphthalene degradation.	Yes	Yes

TABLE 3-2. SUMMARY OF CONTAMINANTS OF CONCERN AND PENTACHLOROPHENOL DEGRADATION PRODUCTS, AUGUST 2010

	Analyte	Naphthalene[1]	Pentachlorophenol[2]	2,4,5-Trichlorophenol	2,4,6-Trichlorophenol	2,4-Dichlorophenol	2-Chlorophenol
	Units	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Sample ID	Sampling Date						
MW-02	8/10/2010	4.5	<4.8	<4.8	<4.8	<4.8	<4.8
MW-03	8/8/2010	<0.2	<1.0	<1.9	<1.9	<1.9	<1.9
MW-04	8/4/2010	<0.2	<1.0	<1.9	<1.9	<1.9	<1.9
MW-05	8/11/2010	**11,800**	**2,860**	66.9	<4.8	42.1	11.1
MW-06	8/5/2010	<0.2	<1.0	<1.9	<1.9	<1.9	<1.9
MW-07	8/4/2010	<0.2	<0.9	<1.9	<1.9	<1.9	<1.9
MW-08	8/8/2010	<0.2	<1.0	<1.9	<1.9	<1.9	<1.9
MW-09	8/8/2010	<0.2	<1.0	<1.9	<1.9	<1.9	<1.9
MW-10	8/11/2010	<1.9	<4.9	<4.9	<4.9	<4.9	<4.9
MW-11	8/4/2010	<0.2	<1.0	<1.9	<1.9	<1.9	<1.9
MW-12	8/10/2010	**1,590**	<4.8	<4.8	<4.8	<4.8	<4.8
MW-13	8/3/2010	<0.2	<0.9	<1.9	<1.9	<1.9	<1.9
MW-14	8/4/2010	<0.2	<1.0	<1.9	<1.9	<1.9	<1.9
MW-17	8/8/2010	<0.2	<1.0	<1.9	<1.9	<1.9	<1.9
MW-18	8/4/2010	<0.2	<0.9	<1.9	<1.9	<1.9	<1.9
MW-19	8/8/2010	<0.2	<1.0	<1.9	<1.9	<1.9	<1.9
MW-20	8/3/2010	<0.2	<1.0	<1.9	<1.9	<1.9	<1.9
MW-22	8/3/2010	0.6	<0.9	<1.9	<1.9	<1.9	<1.9
MW-23	8/5/2010	<0.2	<0.9	<1.9	<1.9	<1.9	<1.9
MW-24	8/4/2010	<0.2	<1.0	<1.9	<1.9	<1.9	<1.9
MW-25	8/5/2010	<0.2	<1.0	<1.9	<1.9	<1.9	<1.9
MW-26	8/5/2010	<0.2	<1.0	<1.9	<1.9	<1.9	<1.9
MW-27	8/3/2010	<0.2	<1.0	<1.9	<1.9	<1.9	<1.9
MW-28	8/9/2010	9.6	<4.8	<4.8	<4.8	<4.8	<4.8
MW-29	8/11/2010	**2,030**	<4.8	<4.8	<4.8	<4.8	<4.8
MW-30	8/11/2010	219	<4.9	<4.9	<4.9	<4.9	<4.9
MW-31	8/5/2010	<0.2	<1.0	<1.9	<1.9	<1.9	<1.9
MW-33	8/3/2010	<1.9	<4.9	<4.9	<4.9	<4.9	<4.9
MW-34	8/8/2010	<0.2	<0.9	<1.9	<1.9	<1.9	<1.9
MW-35	8/9/2010	2.1	<1.0	<1.9	<1.9	<1.9	<1.9
MW-36	8/11/2010	5.2	<4.8	<4.8	<4.8	<4.8	<4.8
SRD-1	8/10/2010	**15,300**	**562**	<4.9	<4.9	<4.9	<4.9
SRD-2	8/2/2010	265	**2,850**	49.1	<4.8	12.8	<4.8
SRD-3	8/10/2010	**517**	<4.8	<4.8	<4.8	<4.8	<4.8

TABLE 3-2. SUMMARY OF CONTAMINANTS OF CONCERN AND PENTACHLOROPHENOL DEGRADATION PRODUCTS, AUGUST 2010

	Analyte	Naphthalene[1]	Pentachlorophenol[2]	2,4,5-Trichlorophenol	2,4,6-Trichlorophenol	2,4-Dichlorophenol	2-Chlorophenol
	Units	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Sample ID	Sampling Date						
SRD-4	8/10/2010	**2,230**	<4.8	<4.8	<4.8	<4.8	<4.8
SRD-5	8/3/2010	**492**	<4.8	<4.8	<4.8	<4.8	<4.8
SRD-6	8/9/2010	<1.9	<4.8	<4.8	<4.8	<4.8	<4.8
SRD-7	8/9/2010	<1.9	<4.8	<4.8	<4.8	<4.8	<4.8
SRD-8	8/9/2010	**2,110**	<4.8	<4.8	<4.8	<4.8	<4.8
SRD-9	8/4/2010	<0.2	<1.0	<1.9	<1.9	<1.9	<1.9
SRD-10	8/2/2010	<0.2	<1.0	<1.9	<1.9	<1.9	<1.9
IRD-1	8/9/2010	3.2	<1.0	<1.9	<1.9	<1.9	<1.9
IRD-2	8/8/2010	<0.2	<0.9	<1.9	<1.9	<1.9	<1.9
IRD-3	8/4/2010	<0.2	<1.0	<1.9	<1.9	<1.9	<1.9
IRD-4	8/3/2010	<0.2	<0.9	<1.9	<1.9	<1.9	<1.9
IRD-5	8/2/2010	<0.2	<0.9	<1.9	<1.9	<1.9	<1.9
IRD-6	8/2/2010	<0.2	<0.9	<1.9	<1.9	<1.9	<1.9
IRD-7	8/3/2010	<0.2	<0.9	<1.9	<1.9	<1.9	<1.9
IRD-8	8/8/2010	<0.2	<1.0	<1.9	<1.9	<1.9	<1.9
SURFACE 1	8/10/2010	<0.2	<1.0	<1.9	<1.9	<1.9	<1.9
SURFACE 2	8/10/2010	<0.2	<1.0	<1.9	<1.9	<1.9	<1.9
SURFACE 3	8/10/2010	<0.2	<1.0	<1.9	<1.9	<1.9	<1.9
SURFACE 4	8/10/2010	<0.2	<1.0	<1.9	<1.9	<1.9	<1.9

Notes:

[1] = Remediation Level 490 µg/L

[2] = Remediation Level 1 µg/L

Bolded values exceed Remediation Levels

TABLE 3-3. NAPTHALENE BIODEGRADATION RATES CALCULATED FROM TIME SERIES DATA

Monitoring Well	Natural Attenuation Rate ($year^{-1}$)	Half-life (years)	R^2	R^2_{crit}	n
MW-02	0.33	2.13	0.58	0.50	7
MW-04	0.51	1.36	0.94	0.77	4
MW-05	0.03 NS	23.10 NS	0.39	0.50	7
MW-12	0.20 NS	3.47 NS	0.20	0.50	7
MW-22	0.28 NS	2.48 NS	0.47	0.57	6
MW-27	0.72	0.96	0.92	0.90	3
MW-29	0.13 NS	5.33 NS	0.56	0.66	5
MW-30	0.17 NS	4.08 NS	0.20	0.77	4
MW-31	0.62	1.12	0.90	0.66	5
MW-33	0.99	0.70	0.99	0.90	3
MW-35	0.67 NS	1.03 NS	0.81	0.90	3
MW-36	0.72	0.96	0.99	0.90	3

Notes:

All natural attenuation rates are statistically significant at $\alpha = 0.05$ except where noted

NS = Not significant

R^2 = Correlation coefficient

R^2_{crit} = Correlation coefficient required for statistical significance

n = Number of values

TABLE 3-4. PENTACHLOROPHENOL BIODEGRADATION RATES CALCULATED FROM TIME SERIES DATA

Monitoring Well	Natural Attenuation Rate ($year^{-1}$)	Half-life (years)	R^2	R^2_{crit}	n
MW-02	0.54	1.28	0.96	0.57	6
MW-04	NA	NA	NA	NA	NA
MW-05	0.03 NS	23.10 NS	0.22	0.90	3
MW-12	0.58	1.20	0.83	0.57	6
MW-22	NA	NA	NA	NA	NA
MW-27	NA	NA	NA	NA	NA
MW-29	NA	NA	NA	NA	NA
MW-30	NA	NA	NA	NA	NA
MW-31	NA	NA	NA	NA	NA
MW-33	0.99	0.70	0.97	0.90	3
MW-35	NA	NA	NA	NA	NA
MW-36	0.95	0.73	0.97	0.90	3

Notes:

All natural attenuation rates are statistically significant at $\alpha = 0.05$ except where noted

NA = Not applicable

NS = Not significant

R^2 = Correlation coefficient

R^2_{crit} = Correlation coefficient required for statistical significance

n = Number of values

TABLE 3-5. EPA BIOSCREEN MODEL INPUT PARAMETERS FOR SIMULATION OF NAPHTHALENE BIODEGRADATION ALONG A PLUME CENTERLINE

Input Category	Input Name	Value	Units	Rationale
1. HYDROGEOLOGY				
	Seepage Velocity (Vs)	150.2	ft/yr	Calculated by BIOSCREEN from other parameters
	Hydraulic Conductivity (K)	6.70E-03	cm/sec	Section 1.1.2 this report
	Hydraulic Gradient (i)	0.0065	ft/ft	Section 1.1.2 this report
	Porosity (n)	0.3	dimensionless	Default
2. DISPERSION				
	Longitudinal Dispersivity (alpha x)	21.0	ft	Calculated by BIOSCREEN from plume length
	Transverse Dispersivity (alpha y)	2.1	ft	Calculated by BIOSCREEN from plume length
	Vertical Dispersivity (alpha z)	0	ft	Calculated by BIOSCREEN from plume length
	Estimated Plume Length (Lp)	700	ft	Figure 3-17 this report
3. ADSORPTION				
	Retardation Factor (RF)	1	dimensionless	Calculated by BIOSCREEN from other parameters
	Soil Bulk Density (rho)	1.7	kg/L	Default
	Partition Coeficient (Koc)	1000	L/kg	Montgomery (2000)
	Fraction of Organic Carbon (foc)	8.60E-06	dimensionless	2010 sampling data
4. BIODEGRADATION				
	1st Order Decay Coefficient (lambda)	0.57	per year	Calculated by BIOSCREEN from half life
	Solute Half-Life (t-half)	1.2	year	Average half-life from significant trends in historical naphthalene concentration data

TABLE 3-5. EPA BIOSCREEN MODEL INPUT PARAMETERS FOR SIMULATION OF NAPHTHALENE BIODEGRADATION ALONG A PLUME CENTERLINE

Input Category	Input Name	Value	Units	Rationale
5. GENERAL				
	Modeled Area Length	650	ft	Distance between MW-12 and MW-13
	Modeled Area Width	200	ft	Figure 3-17 this report
	Simulation Time	56	year	Old process area operation began in 1954 (Arnett 1999), 56 yrs before 2010
6. SOURCE DATA				
	Source Thickness in Sat. Zone	3	ft	Estimated DNAPL thickness
	Source Zones	See Figure 3-17		Arbitrary width; concentration from 2010 data for well MW-12
	Soluble Mass	2000	Kg	Default; 2 metric tons is essentially an infinite source
7. FIELD DATA FOR COMPARISON				
	Concentration	See Figure 3-17	mg/L	Concentrations from 2010 data for wells MW-12, SRD-6, and MW-13
	Dist. from Source	See Figure 3-17	ft	Distance from well MW-12

TABLE 3-6. NATURAL ATTENUATION DIAGNOSTIC SCREENING PARAMETERS

Analyte	Criteria	MW-13	MW-23	MW-28	MW-33	SRD-1	SRD-2
Redox Indicators	**Bold indicates criteria met**						
DO	<0.5 mg/L = anaerobic	**0.13**	**0.41**	1.13	**0**	**0.06**	1.91
Nitrate	<1 mg/L = nitrate reduction	**0.148**	**0.164**	**0.189**	**0.181**	**<0.03**	**<0.03**
Iron (II)	>1 mg/L = iron reduction	0.22	0.71	**2.82**	**3.3**	**3.3**	**3.3**
Sulfate	<20 mg/L = sulfate reduction	35.8	41.6	**11.9**	44.1	36.5	**1.65**
Methane	>0.5 mg/L = methanogenic	0.00111	0.00128	0.014	**1.14**	**0.507**	**3.6**
ORP	< -100 mV = reductive pathway likely	94	110	**-175.5**	-79.6	-83.1	-48.3
Field Parameters	**Bold = favorable**						
pH	5 < pH < 9 favorable to biodegradation	**6.49**	**5.77**	**5.95**	**5.81**	**5.43**	**6.09**
TOC	>20 mg/L = available carbon source	3.64	1.78	5.7	11.5	4.99	19.85
Temp.	>20 ^{o}C = favorable to biodegradation	**26.1**	**24.12**	**28.15**	**24.97**	**28.44**	**24.36**
Alkalinity and Chloride	**Bold indicates elevated concentration**						
Alkalinity (total)	>2x background = mineralization indicator	61.1	50.6	49.3	**128**	**117**	**320**
Chloride	>2x background = mineralization indicator	16.2	13.7	4.21	25	**34.6**	21.2
Microbial Indicators	**Bold = moderate to high (favorable)**						
Anaerobic Pathways							
Dehalococcoides	Anaerobic degradation of CVOCs	1.92E+01	2.14E+01	<2.00E+00	1.48E+02	1.64E+01	2.16E+03
Desulfitobacterium	Anaerobic degradation of PCP	**3.32E+05**	**1.24E+05**	**3.71E+05**	**1.34E+06**	**1.96E+06**	**4.00E+04**
Aerobic Pathways							
PCP Regulator Gene	Aerobic degradation of PCP	6.14E+03	1.56E+03	1.56E+03	**1.42E+04**	1.69E+02	**2.39E+04**
Maleylacetate Reductase	Aerobic degradation of 2,4,6-TCP	2.82E+02	6.36E+01	<4.10E+00	4.06E+02	<1.20E+00	1.19E+03
PCP-4-Monooxygenase	Aerobic degradation of PCP	1.02E+03	1.95E+02	1.53E+02	1.22E+03	<1.20E+00	9.58E+02
Naphthalene Dioxygenase	Aerobic degradation of napththalene	**2.84E+08**	**5.55E+07**	**9.72E+07**	**6.32E+09**	**3.24E+09**	**3.38E+09**

Notes:

Wells MW-33, SRD-1, SRD-2, SRD-3, SRD-4, and SRD-5 are near sources
Wells MW-13, MW-23, MW-28, SRD-7, and SRD-8 are far from sources
Alkalinity background (50.6 mg/L) is from upgradient well MW-23
Chloride background (13.7 mg/L) is from upgradient well MW-23
Duplicate sample was collected from SRD-2. Values are averaged

TABLE 3-6. NATURAL ATTENUATION DIAGNOSTIC SCREENING PARAMETERS

Analyte	Criteria	SRD-3	SRD-4	SRD-5	SRD-6	SRD-7	SRD-8
Redox Indicators	**Bold indicates criteria met**						
DO	<0.5 mg/L = anaerobic	0.9	**0.08**	1.99	**0.18**	**0.32**	2.6
Nitrate	<1 mg/L = nitrate reduction	**<0.03**	**<0.03**	**0.363**	**0.321**	**0.24**	**0.27**
Iron (II)	>1 mg/L = iron reduction	--	--	**3.3**	**3.3**	**2.13**	
Sulfate	<20 mg/L = sulfate reduction	**0.330 J**	**2.14**	**1.41**	**0.230 J**	**2.12**	**0.437**
Methane	>0.5 mg/L = methanogenic	**0.184**	**0.32**	**2.34**	**5.69**	0.00643	**0.467**
ORP	< -100 mV = reductive pathway likely	-30.4	**-104.3**	-93.1	**-100.2**	**-100.7**	**-191.8**
Field Parameters	**Bold = favorable**						
pH	5 < pH < 9 favorable to biodegradation	**6.00**	**6.35**	**6.1**	**6.04**	**6.04**	**6.11**
TOC	>20 mg/L = available carbon source	5.01	5.47	19.5	7.84	4.49	13.5
Temp.	>20 ^{o}C = favorable to biodegradation	**27.55**	**29.91**	**21.52**	**24.17**	**21.69**	**25.4**
Alkalinity and Chloride	**Bold indicates elevated concentration**						
Alkalinity (total)	>2x background = mineralization indicator	**113**	**191**	**531**	**300**	**179**	**168**
Chloride	>2x background = mineralization indicator	21	11.4	13.7	8.79	17.1	18.1
Microbial Indicators	**Bold = moderate to high (favorable)**						
Anaerobic Pathways							
Dehalococcoides	Anaerobic degradation of CVOCs	2.36E+01	6.30E+00	1.16E+02	1.15E+01	8.20E+00	<5.00E-1
Desulfitobacterium	Anaerobic degradation of PCP	**1.70E+06**	**7.55E+04**	**5.82E+04**	**6.13E+04**	**1.91E+06**	6.88E+02
Aerobic Pathways							
PCP Regulator Gene	Aerobic degradation of PCP	7.68E+03	7.18E+02	**4.03E+04**	**4.95E+04**	9.04E+03	2.93E+02
Maleylacetate Reductase	Aerobic degradation of 2,4,6-TCP	3.64E+02	2.06E+01	2.14E+03	3.81E+03	1.13E+02	1.09E+01
PCP-4-Monooxygenase	Aerobic degradation of PCP	1.99E+02	1.23E+01	1.34E+03	1.13E+03	8.74E+02	2.24E+01
Naphthalene Dioxygenase	Aerobic degradation of napththalene	**2.06E+09**	**3.15E+08**	**3.93E+09**	**1.98E+10**	**1.44E+10**	**4.07E+07**

Notes:

Wells MW-33, SRD-1, SRD-2, SRD-3, SRD-4, and SRD-5 are near sources
Wells MW-13, MW-23, MW-28, SRD-7, and SRD-8 are far from sources
Alkalinity background (50.6 mg/L) is from upgradient well MW-23
Chloride background (13.7 mg/L) is from upgradient well MW-23
Duplicate sample was collected from SRD-2. Values are averaged

FIGURES

Texarkana Wood Preserving Company Site
Texarkana, Bowie County,Texas

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Figure 1-1. Site Map
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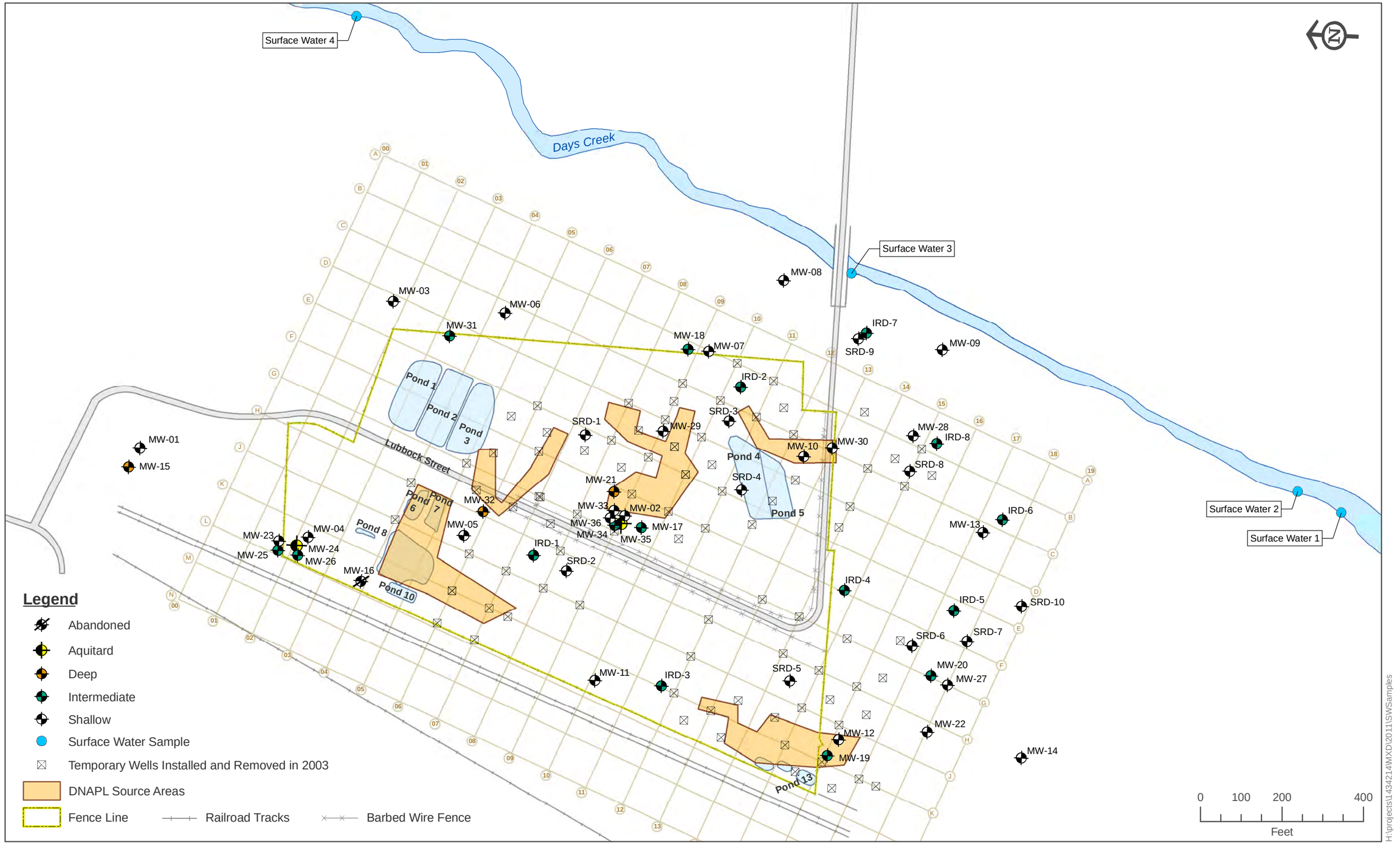

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Figure 1-2. Location of Monitoring Wells and Surface Water Samples
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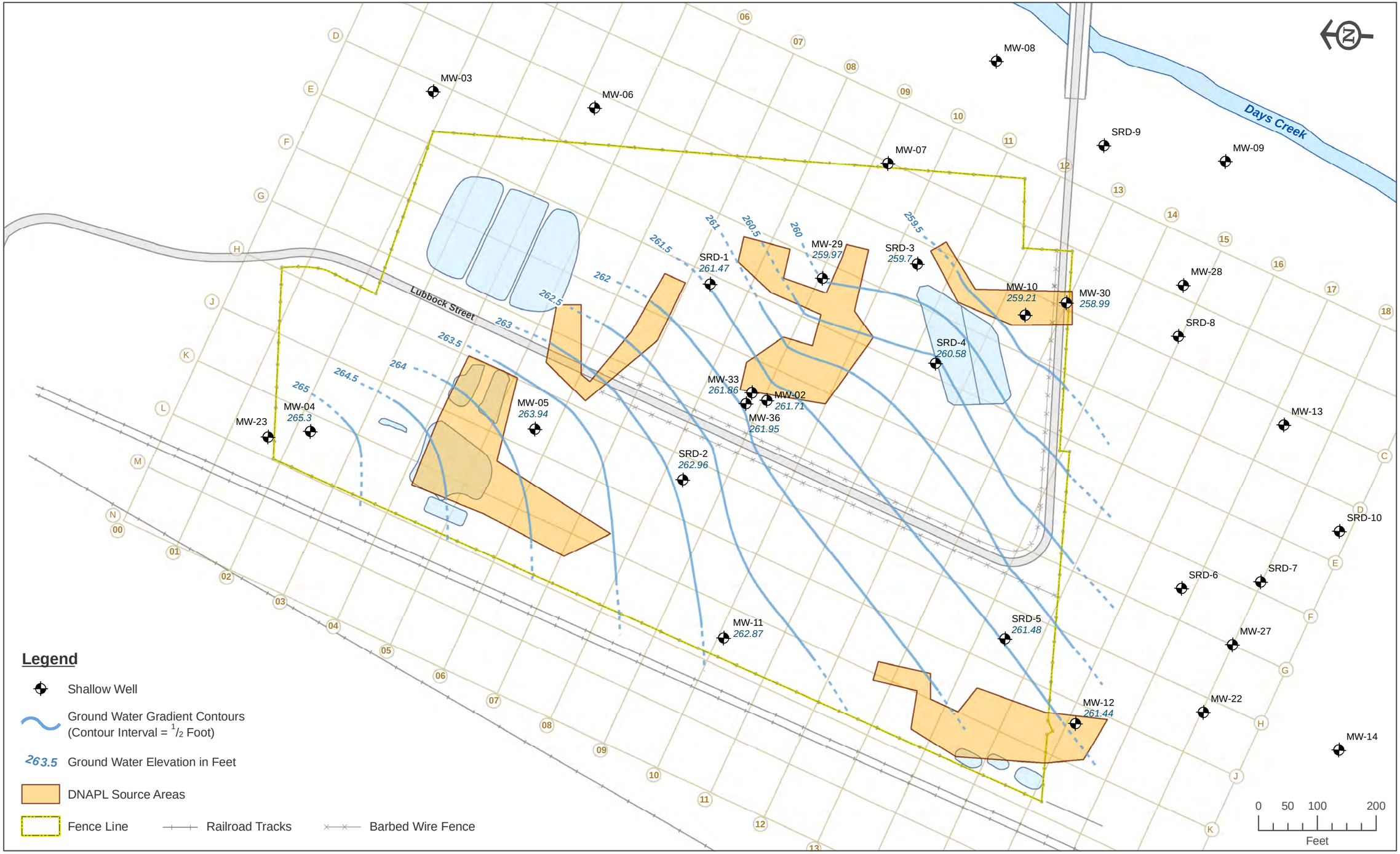

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Figure 1-3. Potentiometric Surface Map of the Shallow Water Bearing Zone - August 2010
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Notes:
- All sample results are presented in micrograms per liter (µg/L)
- Plume contours are based on results of a 2003 sampling event presented in the Supplemental Remedial Investigation (EA, 2008)

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Figure 3-1. Naphthalene Shallow Water Bearing Zone Ground Water Sample Results (October 2003, November 2007, and August 2010)
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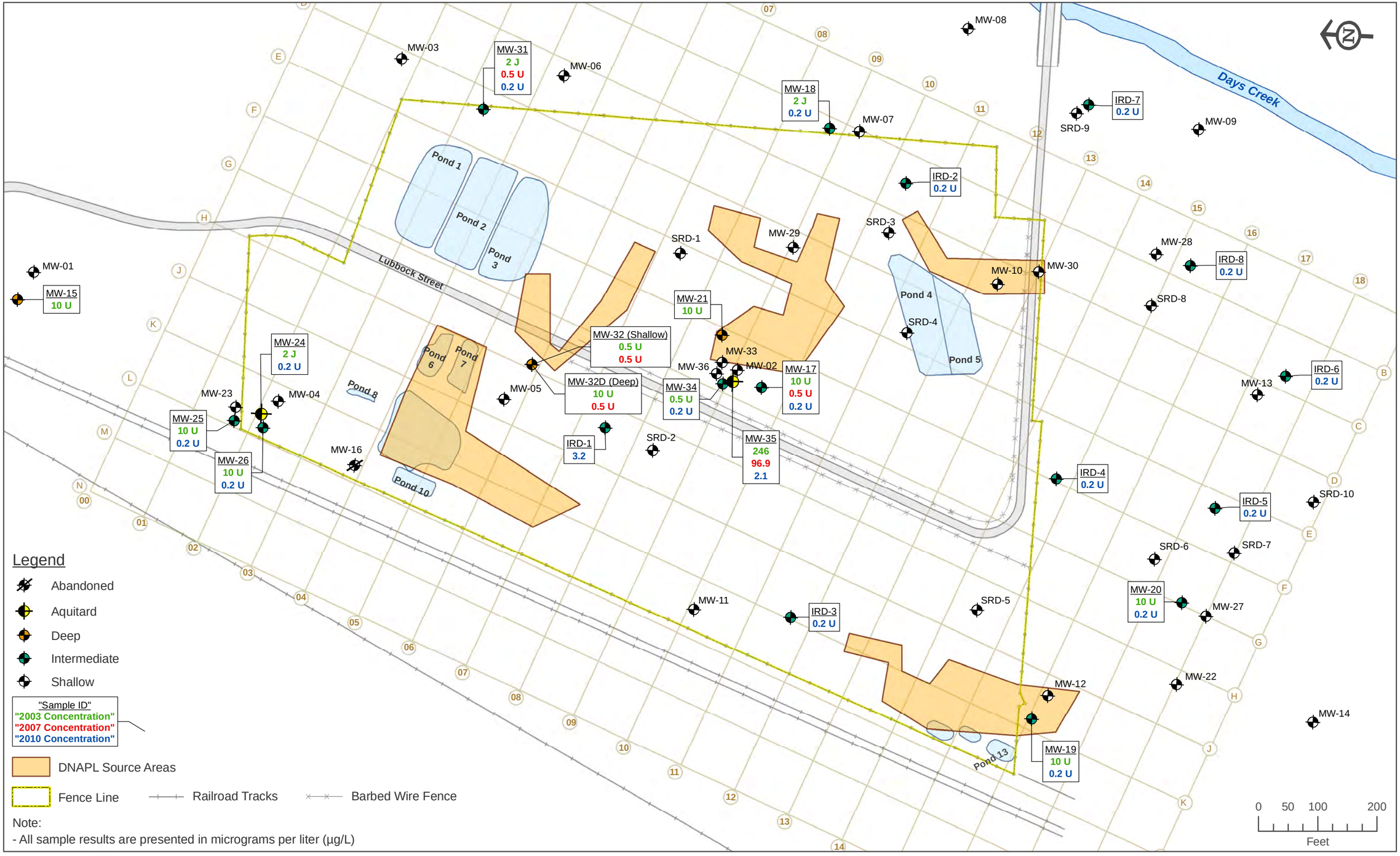

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Figure 3-2. Naphthalene Aquitard, Intermediate, and Deep Water Bearing Zone Ground Water Sample Results (October 2003, November 2007, and August 2010)
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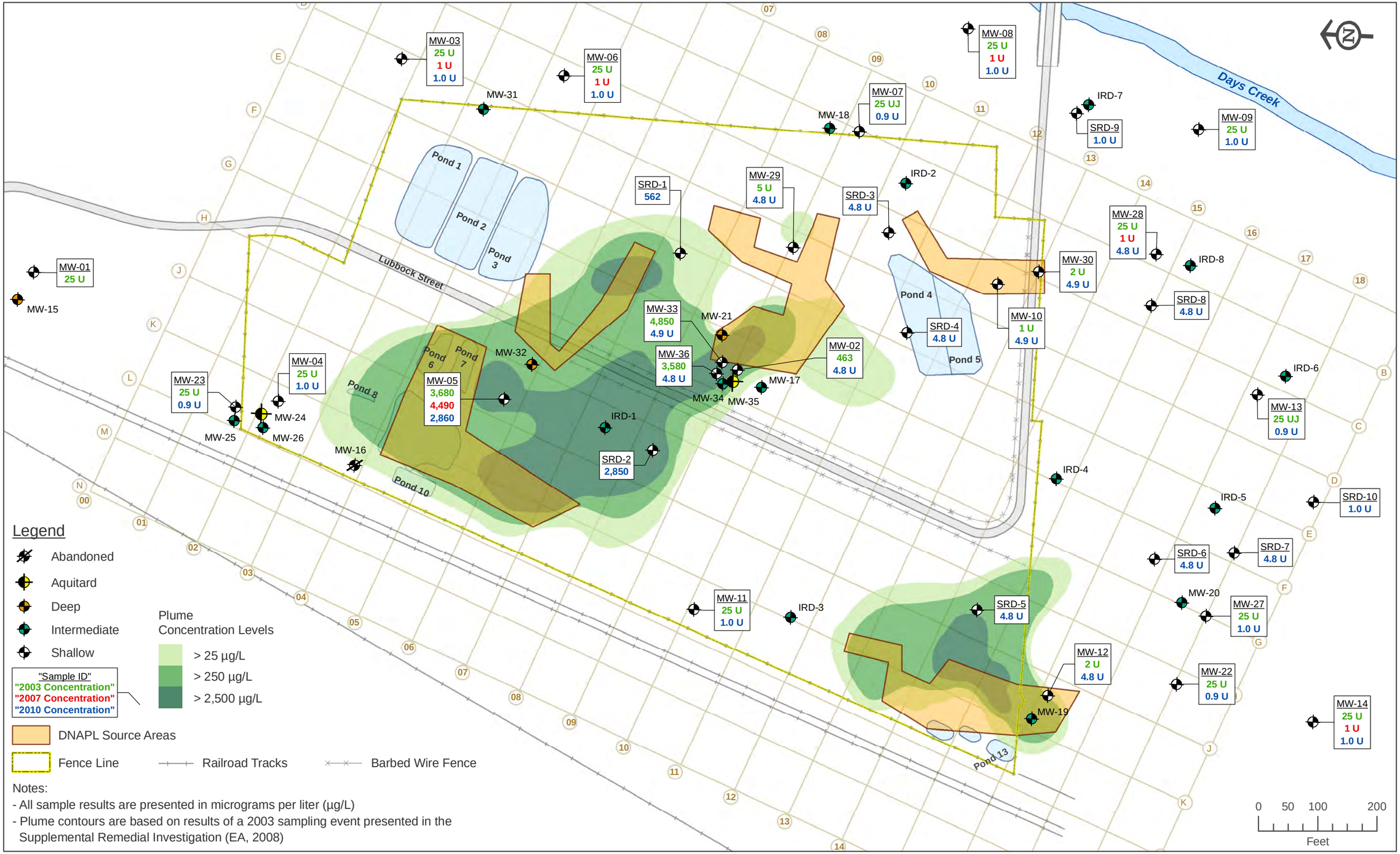

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Figure 3-3. Pentachlorophenol Shallow Water Bearing Zone Ground Water Sample Results (October 2003, November 2007, and August 2010)
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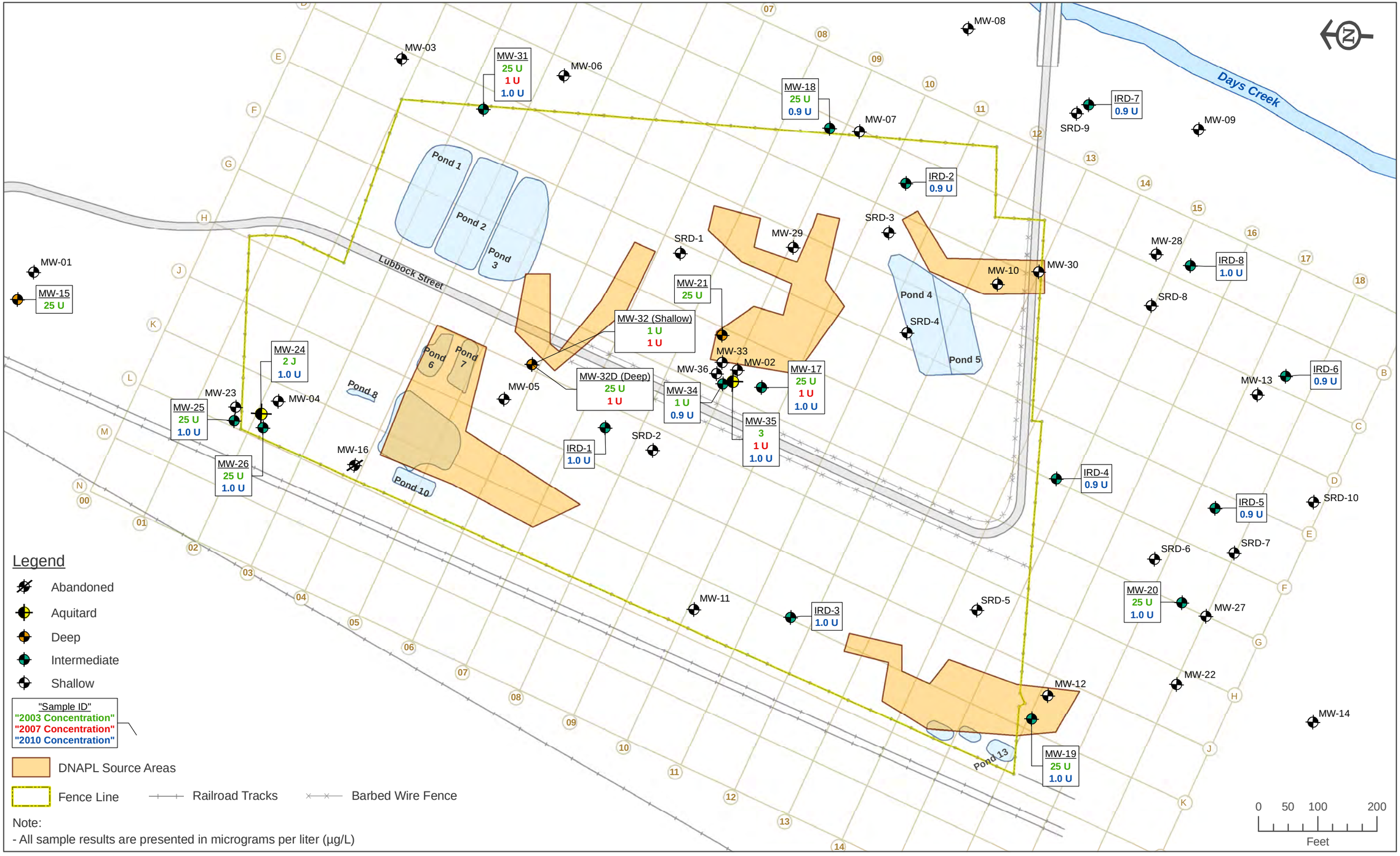

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Figure 3-4. Pentachlorophenol Aquitard, Intermediate, and Deep Water Bearing Zone Ground Water Sample Results (October 2003, November 2007, and August 2010)
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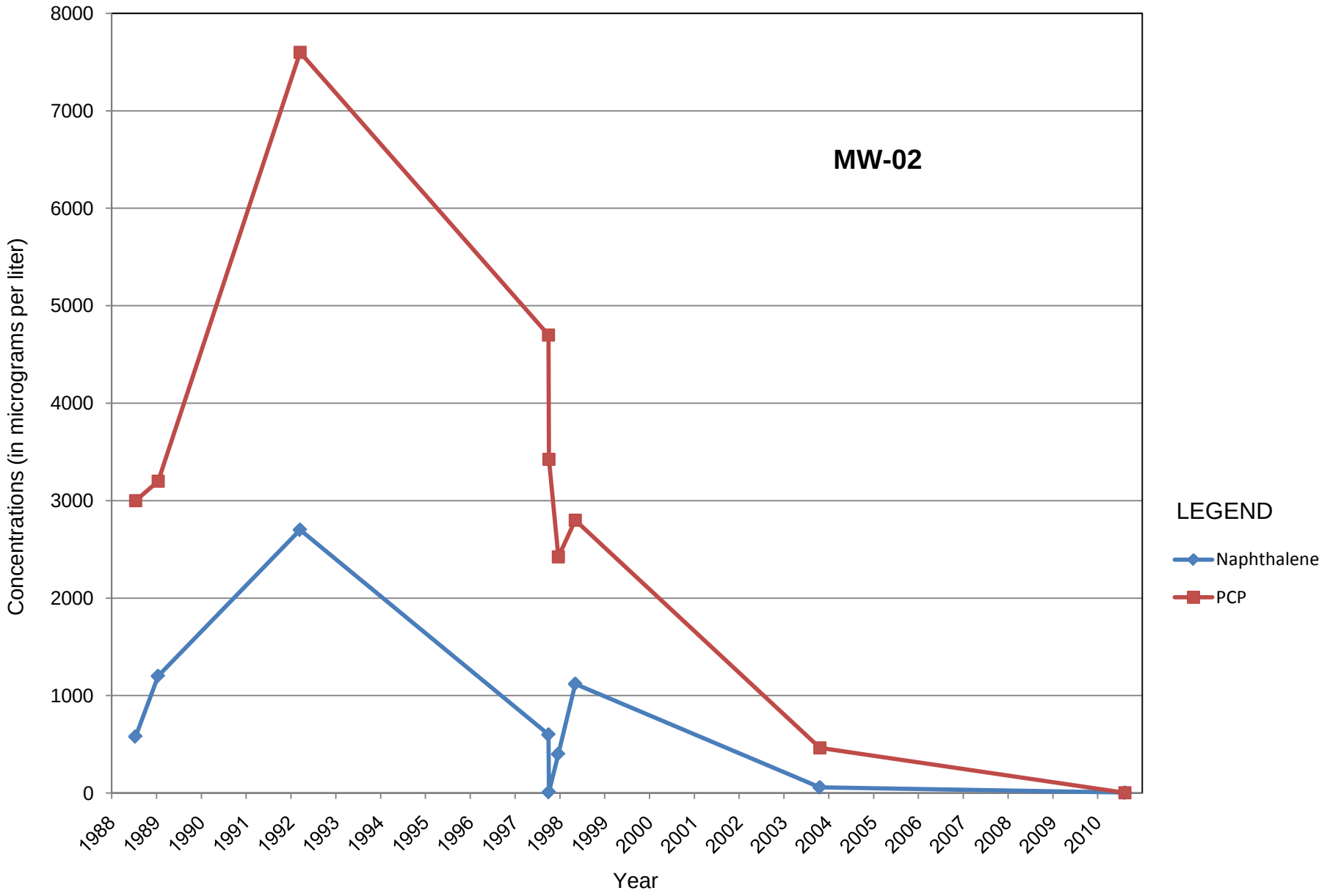

Figure 3-5. Temporal Changes in Concentrations of Naphthalene and PCP, Well MW-02
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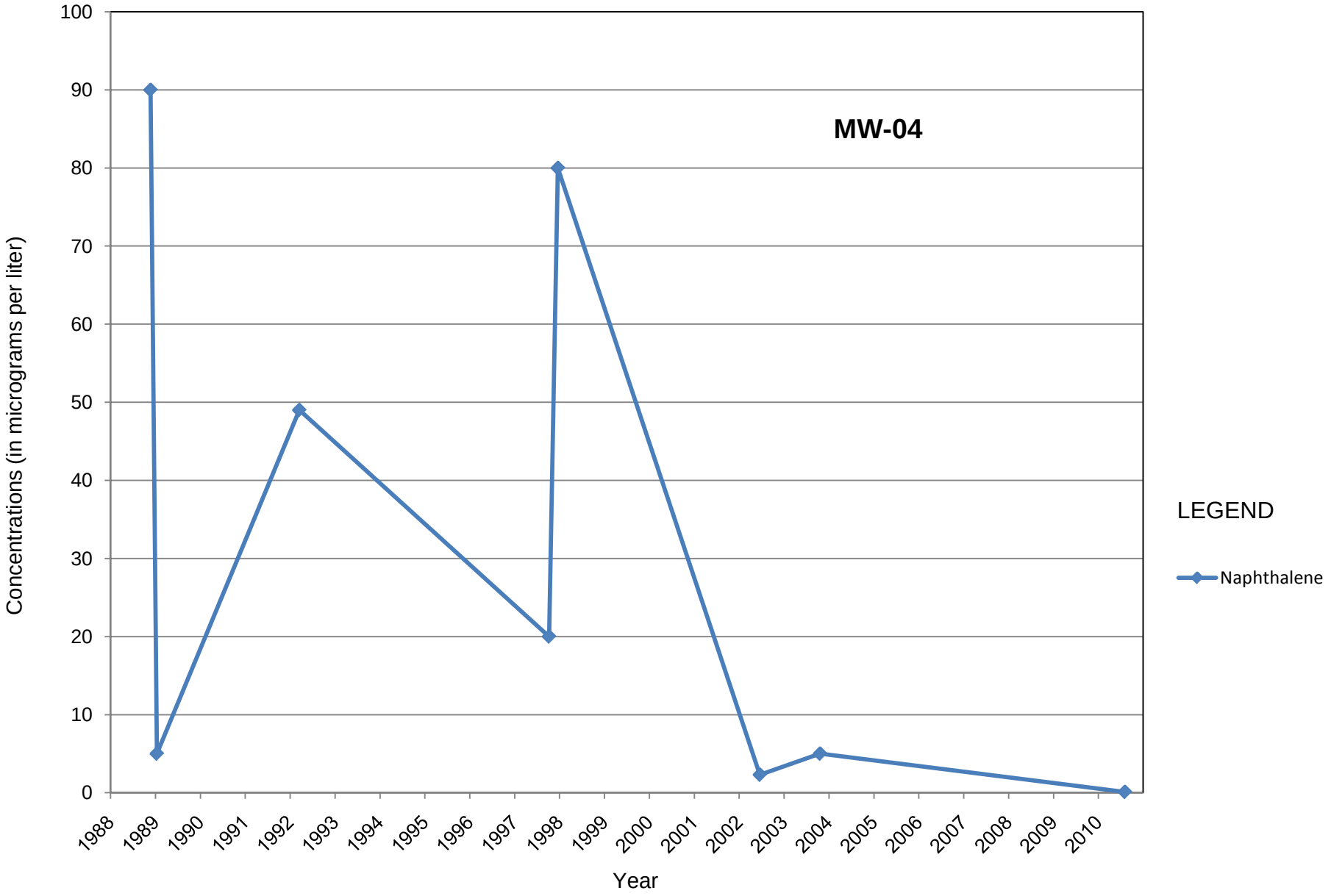

Figure 3-6. Temporal Changes in Concentrations of Naphthalene, Well MW-04
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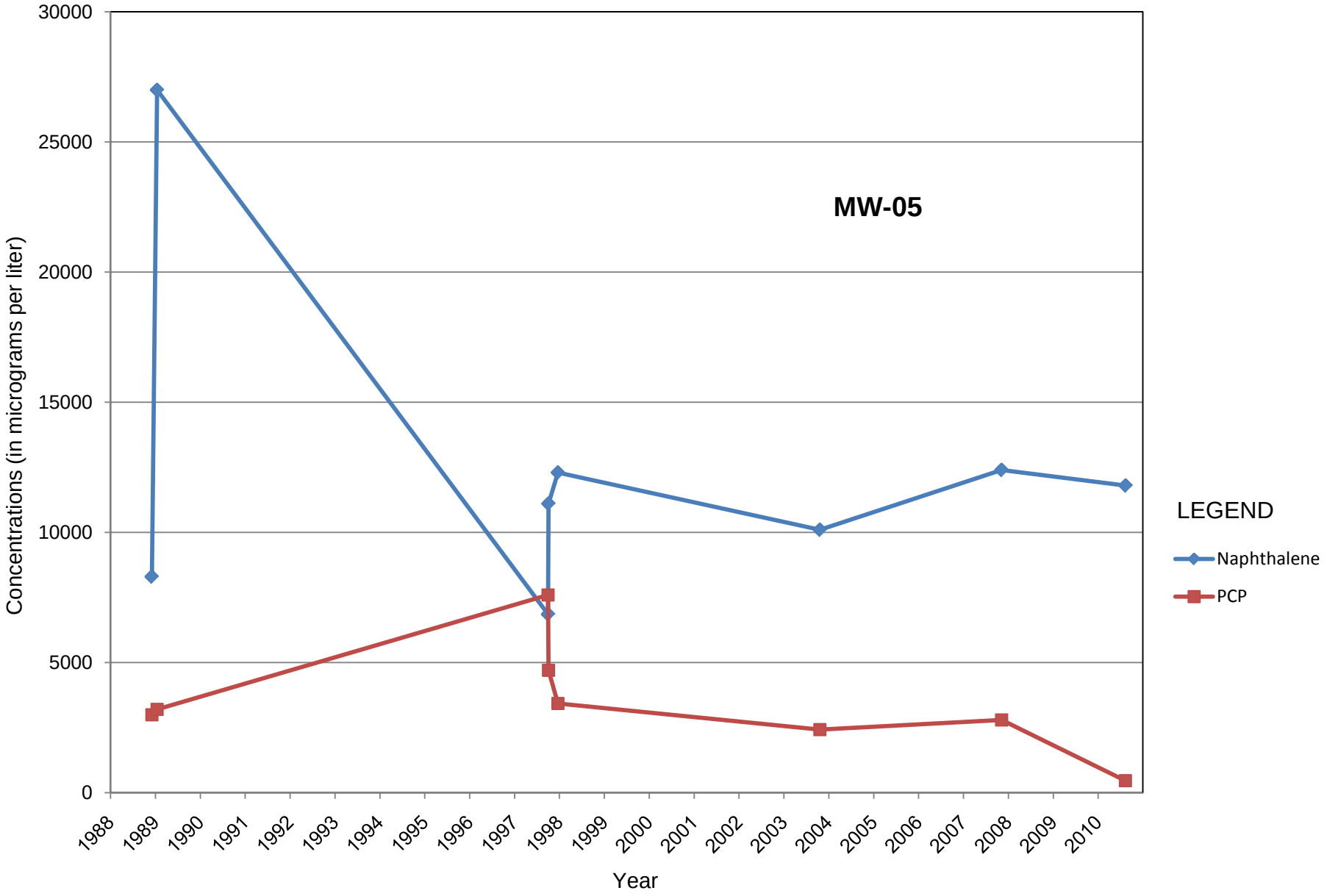

Figure 3-7. Temporal Changes in Concentrations of Naphthalene and PCP, Well MW-05
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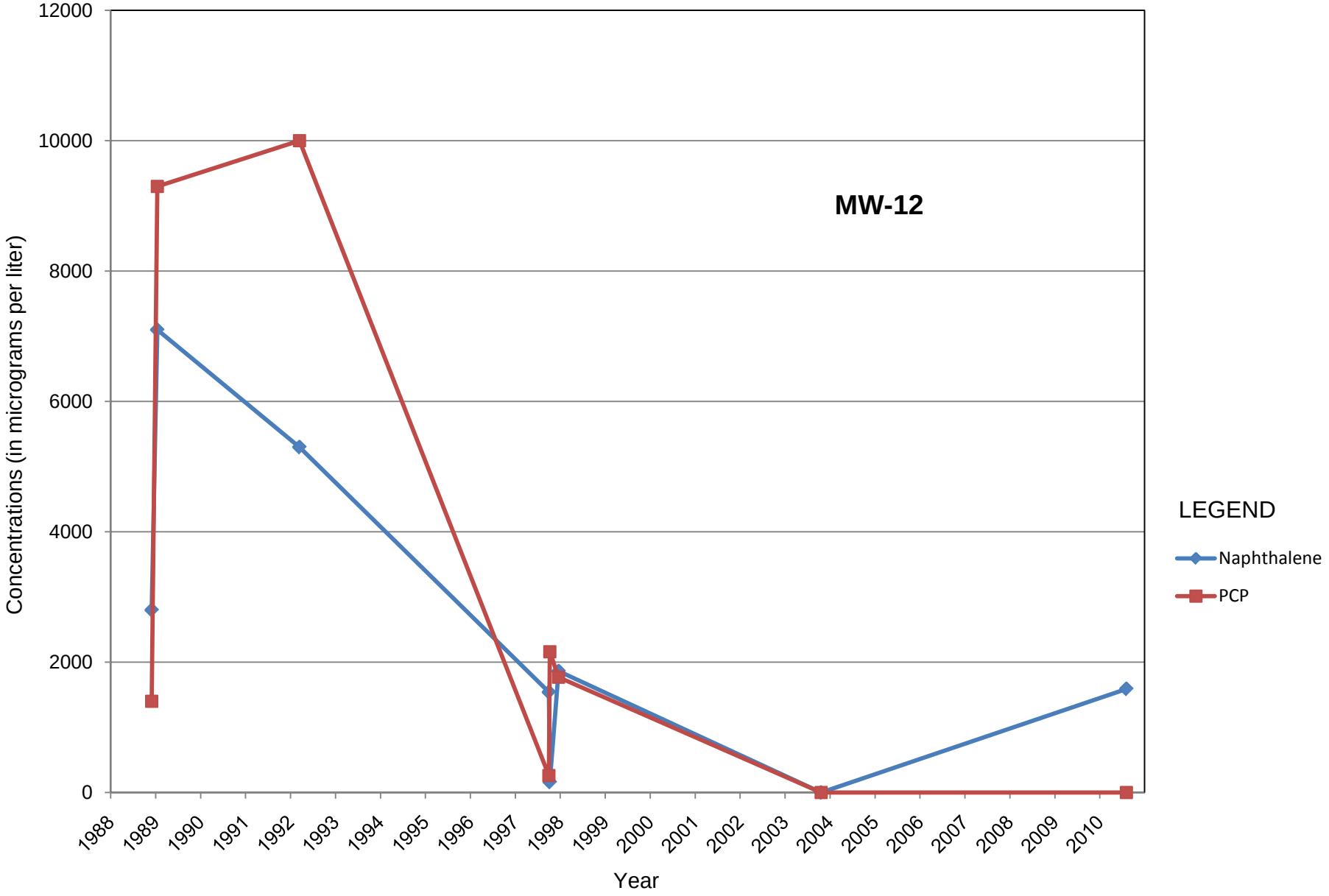

Figure 3-8. Temporal Changes in Concentrations of Naphthalene and PCP, Well MW-12
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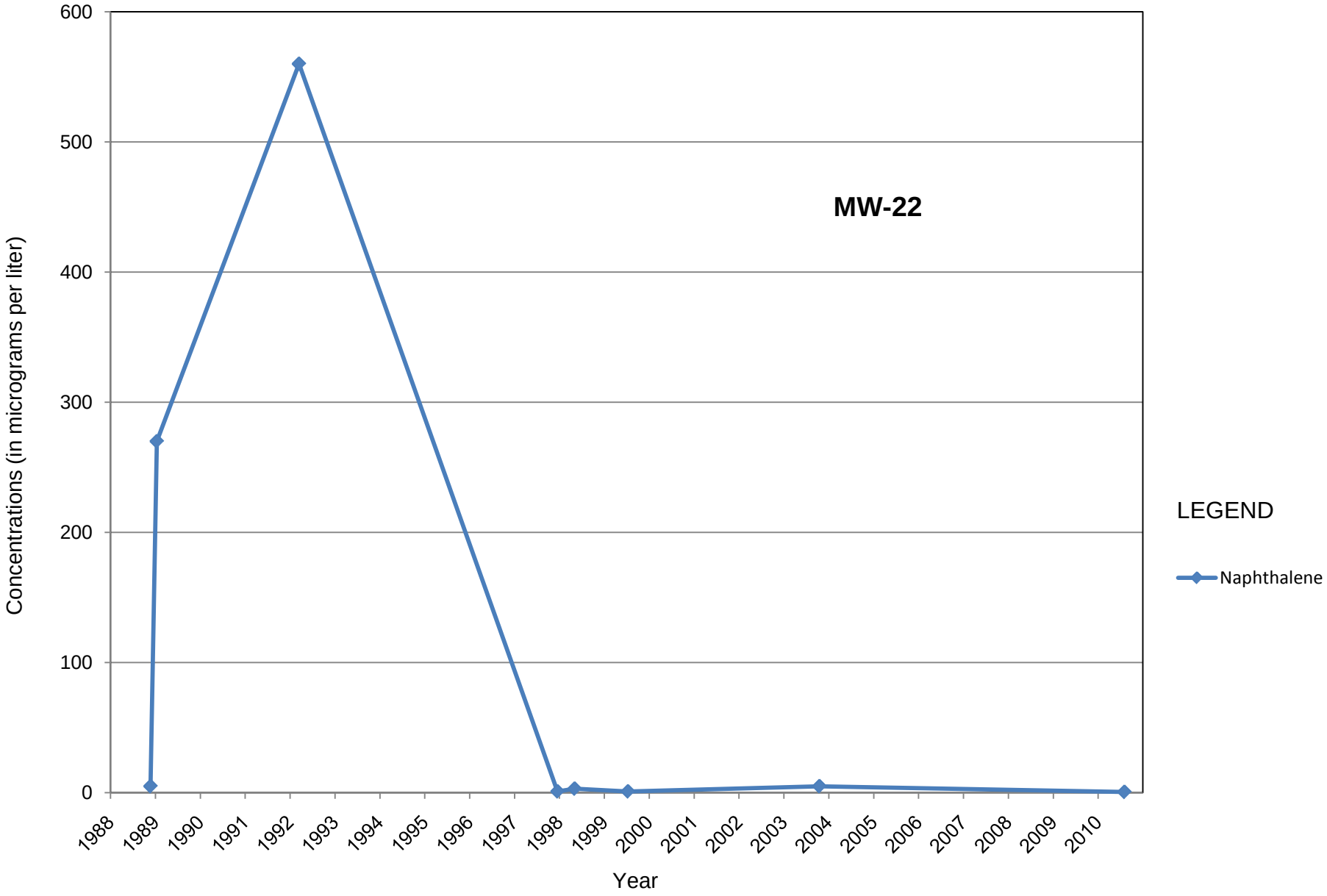

Figure 3-9. Temporal Changes in Concentrations of Naphthalene, Well MW-22
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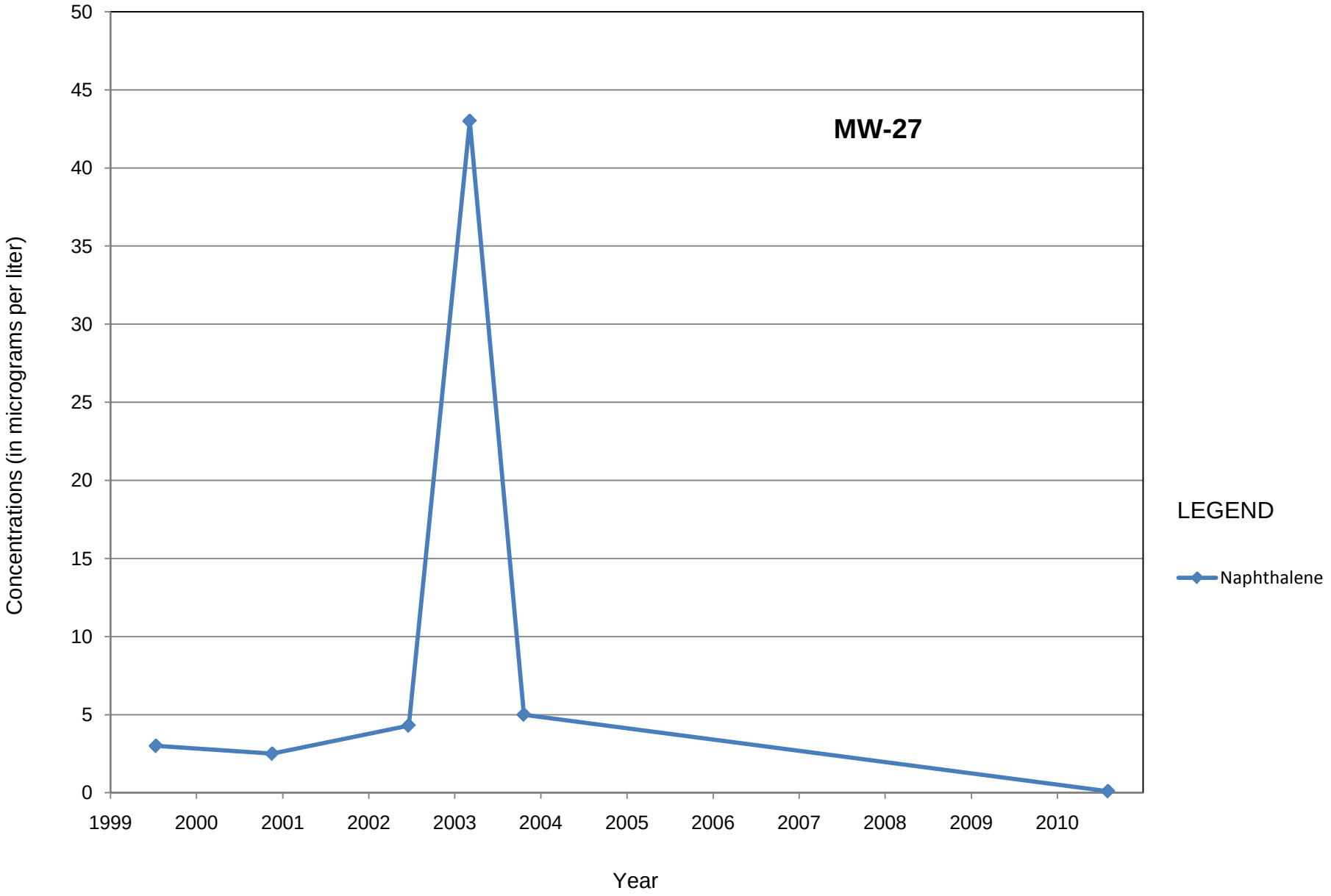

Figure 3-10. Temporal Changes in Concentrations of Naphthalene, Well MW-27
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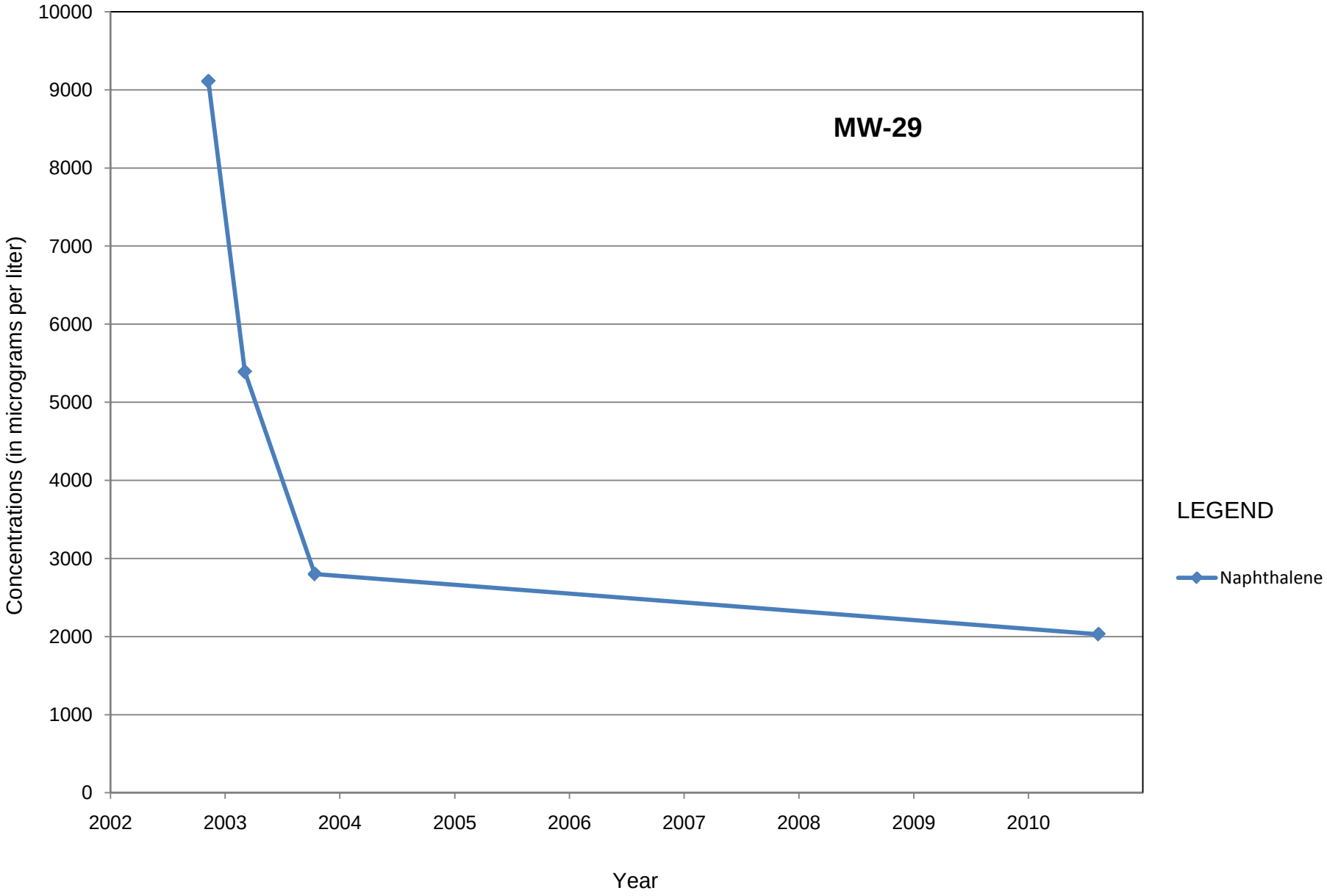

Figure 3-11. Temporal Changes in Concentrations of Naphthalene, Well MW-29
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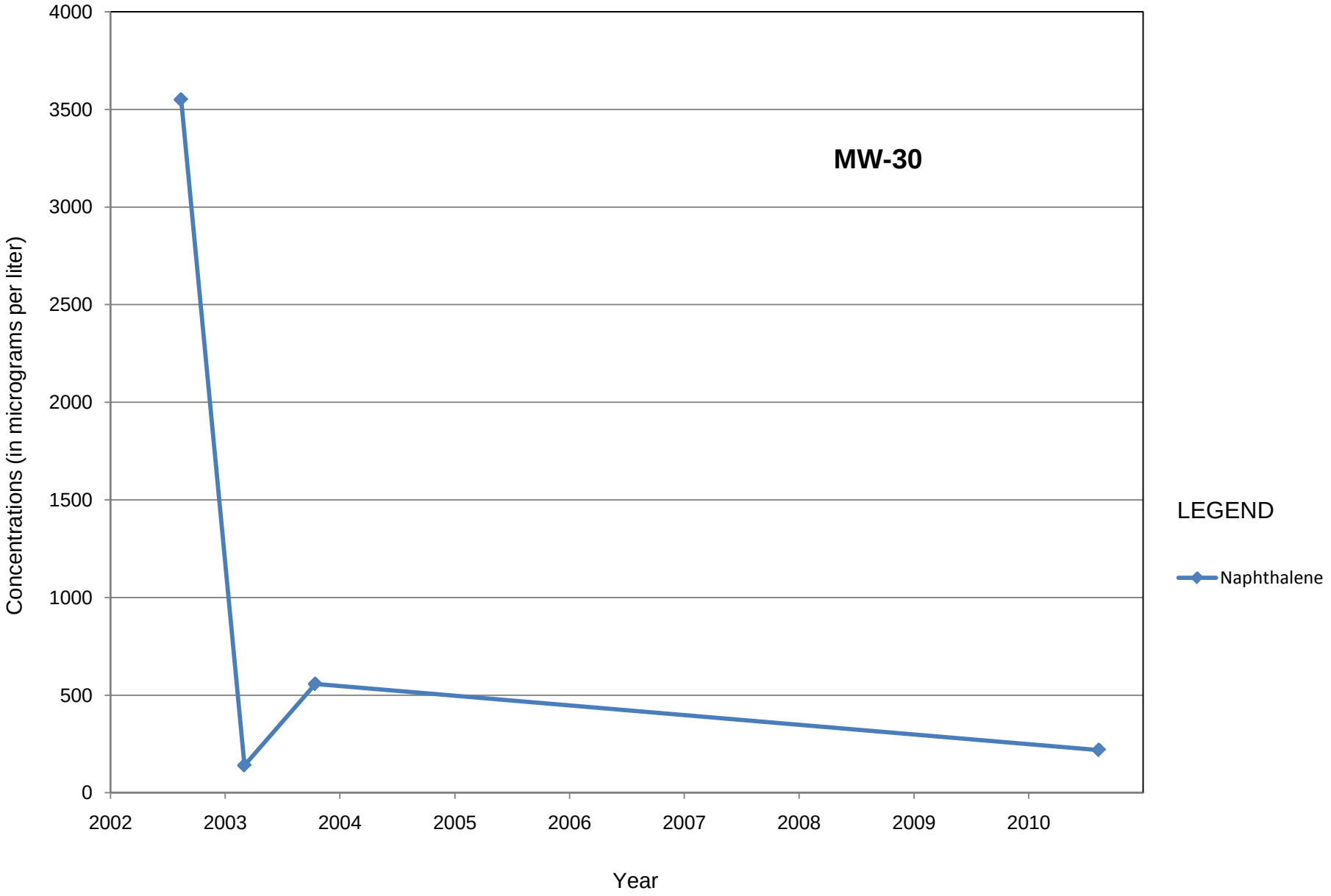

Figure 3-12. Temporal Changes in Concentrations of Naphthalene, Well MW-30
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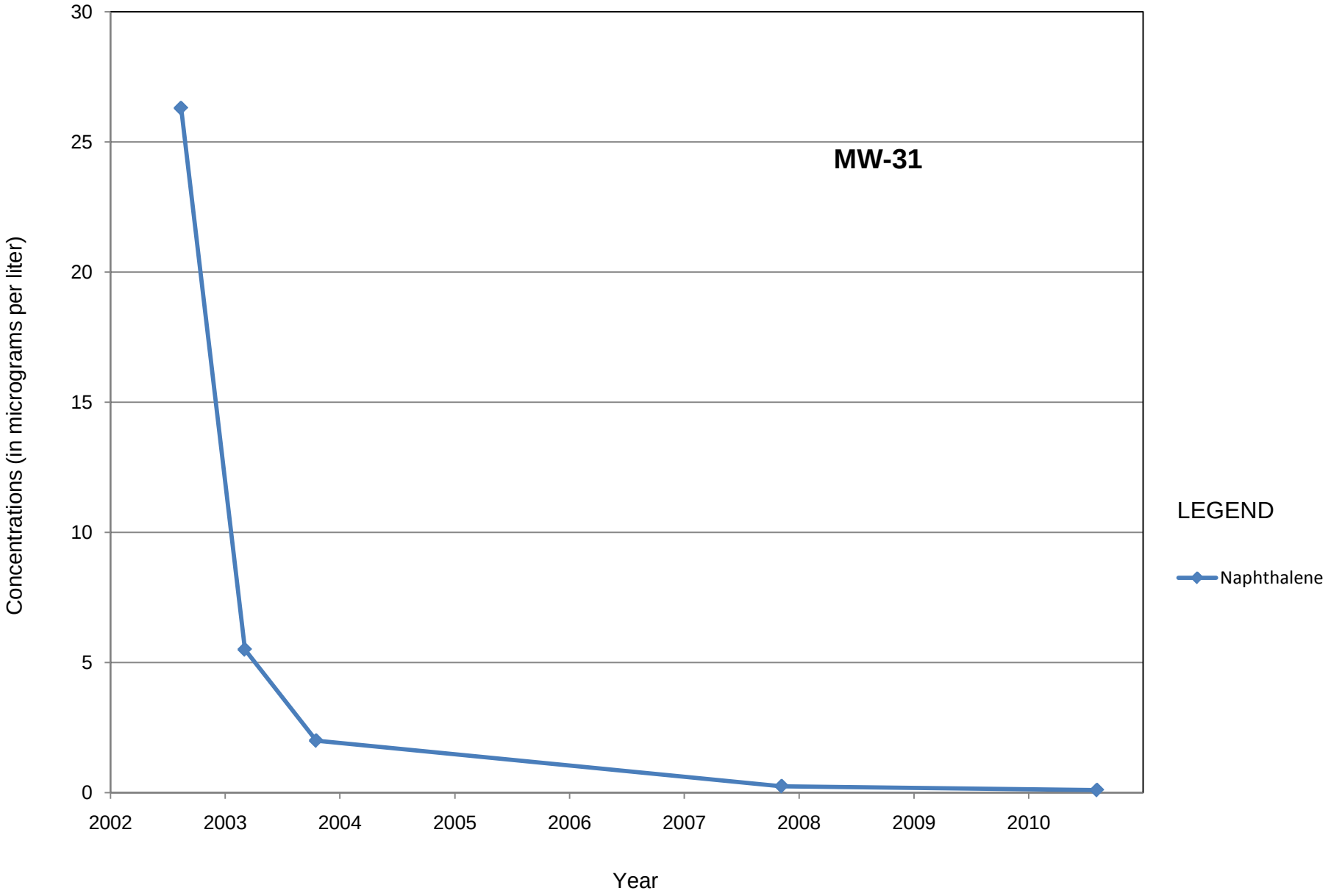

Figure 3-13. Temporal Changes in Concentrations of Naphthalene, Well MW-31
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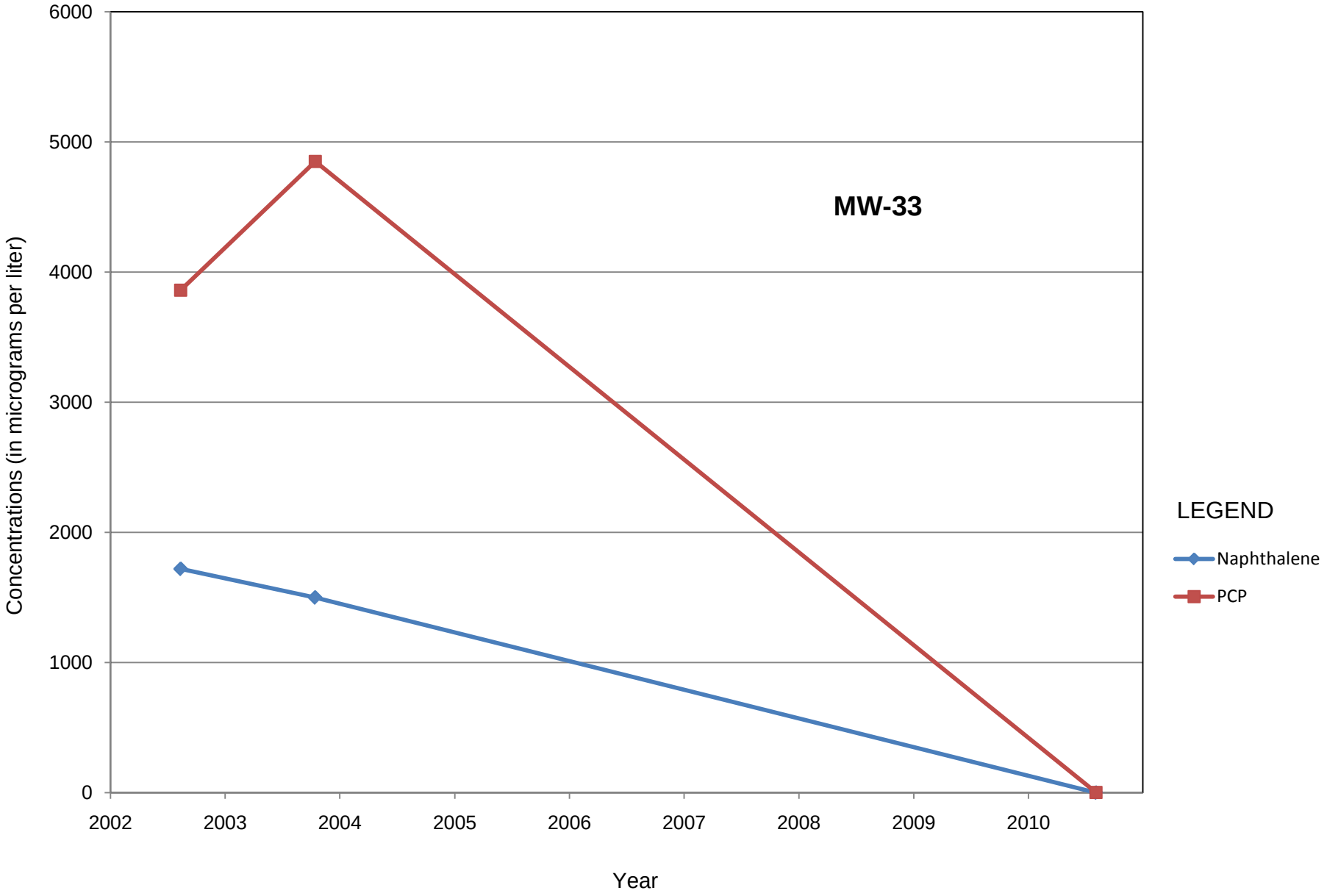

Figure 3-14. Temporal Changes in Concentrations of Naphthalene and PCP, Well MW-33
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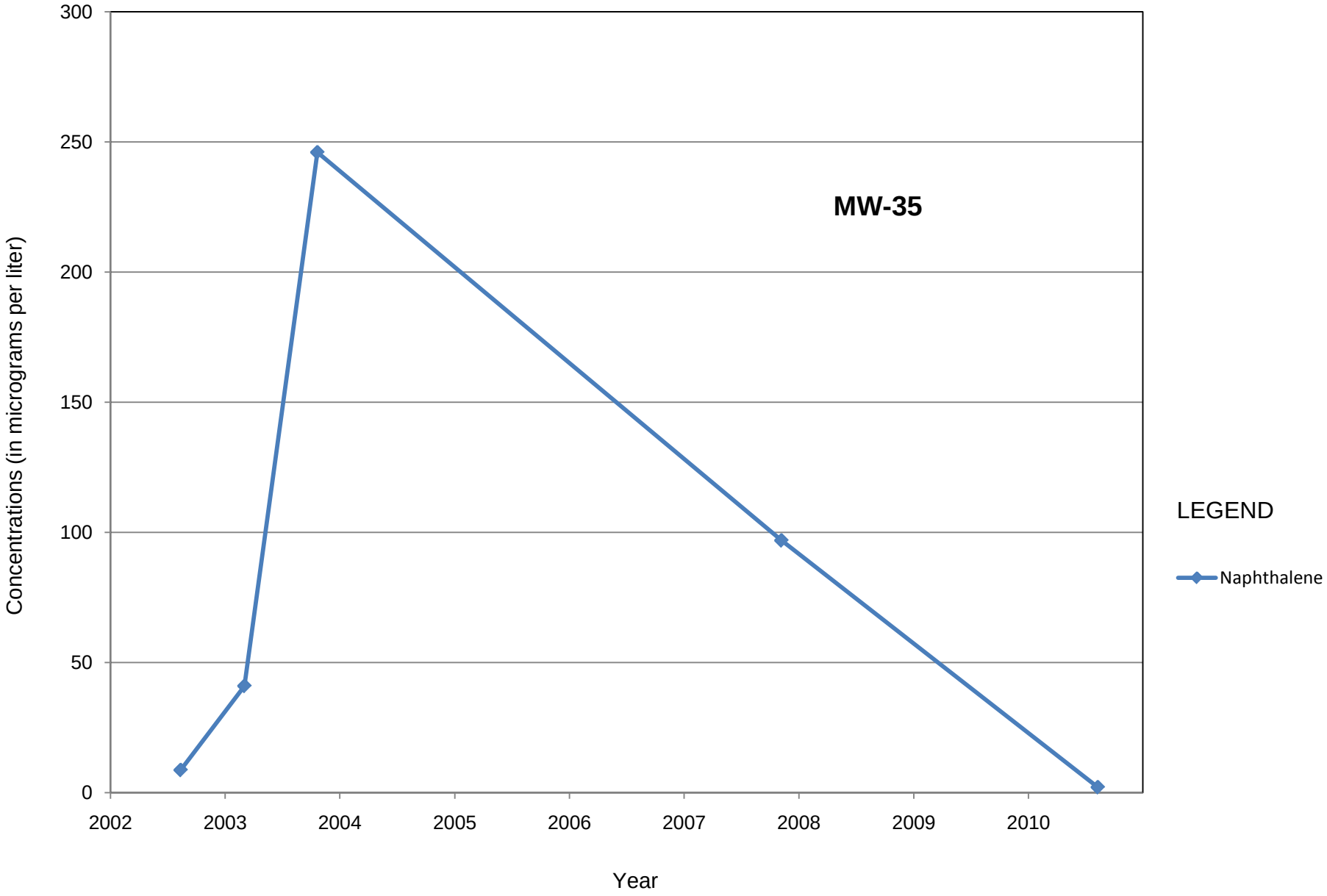

Figure 3-15. Temporal Changes in Concentrations of Naphthalene and PCP, Well MW-35
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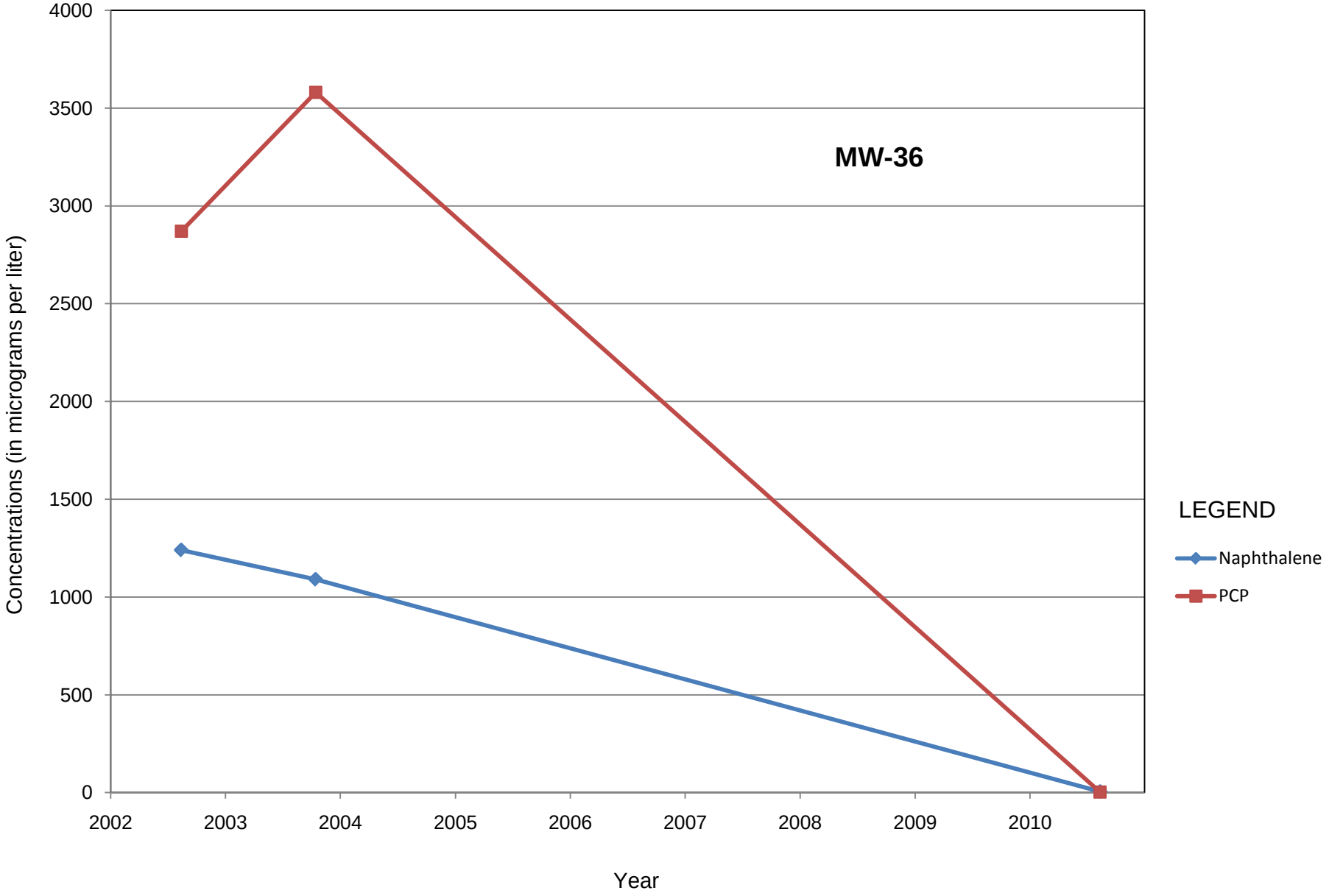

Figure 3-16. Temporal Changes in Concentrations of Naphthalene and PCP, Well MW-36
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Figure 3-17. BIOSCREEN Simulation Area
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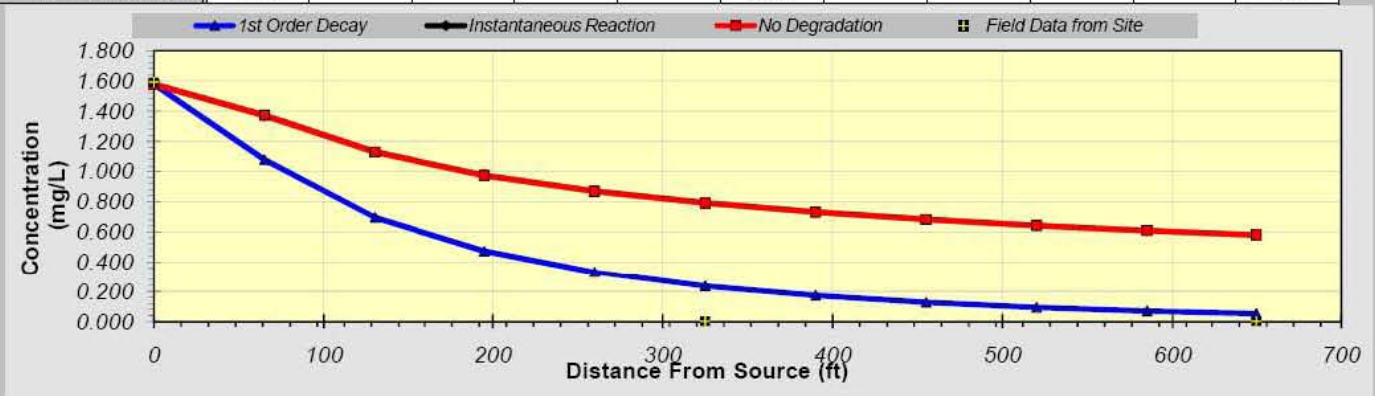
DISSOLVED HYDROCARBON CONCENTRATION ALONG PLUME CENTERLINE (mg/L at Z=0)

TYPE OF MODEL	Distance from Source (ft) 0	65	130	195	260	325	390	455	520	585	650
No Degradation	1.577	1.372	1.129	0.975	0.869	0.791	0.731	0.683	0.643	0.609	0.581
1st Order Decay	1.577	1.078	0.697	0.473	0.331	0.237	0.172	0.126	0.093	0.070	0.052
Inst. Reaction	1.577	1.372	1.129	0.975	0.869	0.791	0.731	0.683	0.643	0.609	0.581
Field Data from Site	1.590					0.002					0.002



Calculate Animation

Time: 56 Years

Return to Input

Recalculate This Sheet

Figure 3-18. Output from BIOSCREEN Simulation for Naphthalene using Average Degradation Rate from Temporal Trends
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