Fate of Chlorinated Compounds in a Sedimentary Fractured Rock Aquifer in South Central Wisconsin

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

A study was carried out in a sedimentary fractured rock site located in south central Wisconsin, US, which was impacted by DNAPL releases estimated to occur in the 1950's and 1960's. The majority of the DNAPL has accumulated in the upper portion of the Lone Rock Formation at a depth between 140 and 180 ft bgs referred as Layer 5 in this study. A groundwater VOC plume of more than 3km long has formed in this Layer. The DNAPL is mainly composed of 1,1,1-TCA, PCE, TCE and BTEX, while large amounts of biodegradation products such as cis-DCE and 1,1-DCA are present in the plume.

Long term VOC data have been collected at the site and diverse geological and hydrogeological techniques have been applied to have a better understanding of the DNAPL history and behavior of the VOC plume. Evidence of biodegradation was also documented near the DNAPL source in these studies. The thesis objectives of the present study aimed first to have a better understanding of the long term contaminant distribution and degradation history at the site. This objective was accomplished reviewing the VOC historical concentration data collected from 1992 to 2006 in the wells tapping the most contaminated. hydrogeological unit in the bedrock (Layer 5) and in the overburden aquifer (referred as Layer 2). The second objective aimed to evaluate the current degree or extent of biodegradation of chlorinated compounds, which was accomplished evaluating the current groundwater redox conditions and using a combined analysis of VOC concentration and carbon isotope data collected in groundwater in September 2007.

The historical data collected between1992 to 2006 showed the degradation of the VOC plume in Layer 5 was controlled by the availability of electron acceptors and redox conditions in the fracture bedrock aquifer. This pattern and the extension of the VOC

plume were linked to different DNALP pumping events in the source zone and the operation of a Hydraulic Barrier System.

The current geochemical and isotope study showed a different pattern of biodegradation of chlorinated compounds in different parts of the plume. The cis-DCE tend to accumulate in the area from the source to the middle of the plume and around 80 % of biodegradation of 1,1,1-TCA to 1,1-DCA was observed in this area. The fringes of the plume were characterized by a dominant presence of TCE and 1,1,1 TCA. These patterns were linked to different redox conditions and amount of electron acceptors. The cis-DCE dominated area is characterized by anaerobic conditions and the presence of relative high amount of BTEX. The TCE-dominated area is under aerobic condition and no BTEX was found in this area. The operation of the Hydraulic Barrier System seems to have change redox condition which influenced the extent of degradation in the plume, especially in the area between the extraction wells. The formation of large amounts of VC in Layer 2 and the more reducing (at least sulfate reducing and maybe methanogenic conditions) of the groundwater in this Layer compared to Layer 5 confirmed the extent of VOC biodegradation is linked to the availability of electron donors.

This study provides information about the current degree of the biodegradation of chlorinated compounds at a fracture rock site. This information is very valuable for the evaluation of natural attenuation as strategy for long term plume management or for future remediation strategies such as biostimulation or bioaugmentation at the site. This study also shows the present and long term behavior of the chlorinated compounds (degradation history) in the most contaminated hydrogeologic unit (Layer 5), has mainly been controlled by plume management strategies including DNAPL pumping in the source and the creation of a Hydraulic Barrier System. The ketones and BTEX, that acted

as electron donors and carbon substrate for the microbial community responsible for the dechlorination of chlorinated compounds were shown to have controlled the past and current redox conditions and thus the degree and potential of biodegradation of chlorinated ethenes and chlorinated ethanes at the study site.

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1 Introduction

Chlorinated compounds, usually used as industrial solvents, were first produced in the United States in 1906. The significant use in the manufacturing industry began during World War II (Pankow et al., 1996) and increased dramatically in the 50's, 60's, and 70's. Chlorinated solvents were first recognized as contaminants in groundwater in the late 70's, but the problem was not widely recognized until 1981 (Pankow et al., 1996). Perchloroethylene (PCE) and trichloroethylene (TCE), the two heaviest chlorinated ethenes, are widely used for dry cleaning of fabrics and metal degreasing. PCE and TCE contamination has been observed extensively in the US and they are among the most common volatile organic contaminants (VOCs) (USEPA, 1999). 1,1,1-Trichloroethane (1,1,1-TCA), a chlorinated ethane, was until recently widely used as an industrial solvent. In the United States, 1,1,1-TCA has been found as a contaminant in at least 459 sites (30 percent of total) designated to the National Priorities List (NPL) by the US Environmental Protection Agency (EPA) (Grostern and Edwards, 2006).

PCE and TCE have both been identified as possible carcinogens. The USEPA has set drinking Maximum Contaminant Level (MCL) for them at 5 μg/L due to the health risks upon exposure (USEPA, 2002). The MCL for 1,1,1-TCA has been set at 0.2 mg/L, which is relatively high, because EPA believes this is the lowest level that is achievable for remediation given current technology and resources (USEPA, 2002).

There have been many studies conducted on chlorinated compounds in granular aquifers. However, studies on chlorinated compounds in fractured rock aquifers are limited. The following sections are intended to review the literature on fractured rock systems, degradation of chlorinated compounds, and stable carbon isotopes to serve as the background for this study on the fate of chlorinated compounds in a sedimentary fractured rock aquifer using carbon isotopes as a tool.

1.1 VOCs in Fractured Rock Aquifers

Fractured rock aquifers are ubiquitous throughout North America and are of particular interest because of their important role for water supply. Investigating fractured rock aquifers is relatively difficult due to the complexity of the fractures. Depth-discrete instrumentation is often required for aquifer characterization and groundwater sampling. Studies have been conducted on the groundwater flow, contaminant transport, DNAPL migration, plume formation, and VOCs degradation in fractured rock aquifers.

Characteristics of the fractures and groundwater flow pattern in fractures are the starting point for any hydrogeological studies in fractured rock aquifers. Studies suggest that the fractures are the main conduit for groundwater flow and contaminant transport (Berkowitz, 2002; Cooke et al., 2006; Lapcevic et al., 1999), but depending on the type of the rock, the matrix can also contribute significantly.

DNAPL migration and accumulation in fractured rock aquifers are controlled by many factors including fracture setting, matrix porosity, capillary entry pressure, groundwater flow, and bedrock inclination. Kueper and McWhorter (1991) examined the conditions under which DNAPL would enter an initially water-saturated, rough-walled fracture. They conducted simulations, which showed that the DNAPL would migrate through the larger aperture regions of a fracture plane and the DNAPL had the potential to enter progressively smaller aperture fractures with depth as it migrated. Wolfe and Haugh (2001) listed five conceptual models for DNAPL accumulation in karst settings to help differentiate DNAPL accumulation mechanisms under different circumstances. Parker (1994) proposed that molecular diffusion of organic contaminants from DNAPL into the matrix could be an important process that controls the mass distribution of organic contaminants in fractured porous geologic media.

There have been many investigations on the formation of contaminant plumes in fractured rock aquifers, though few papers were published. Processes such as advection, diffusion, and sorption control the development of the plumes, among which diffusion is especially important in sedimentary rock aquifers. Meyer (2005) found that the contaminant plume was substantially retarded due to diffusion of contaminants into the matrix in this sedimentary rock aquifer. In a study by Chapman and Parker (2005), back diffusion from matrix was found to cause persistent plume even after DNAPL removal or isolation. Back diffusion was demonstrated again in another study by Parker et al. (2006a). In this study a halogenated organic herbicide plume containing metolachlor (MET) and TCE was discovered in 1992 in a fractured dolostone aquifer that was used for municipal water supply in Southern Ontario. The plume was believed to be formed by reverse diffusion from the rock matrix into the fractures, causing a low concentration but persistent plume of MET and TCE with no significant concentration decrease since 1993.

Published field studies on the degradation of chlorinated solvents in fractured rock aquifers are sparse (Table 1-1). These studies were conducted in various rock types including dolomite (Yager et al., 1997), basalt (Mobarry et al., 1999), karst deposits (Byl and Williams, 2000), shale (Lenczewski et al., 2003), and sandstone (Pierce, 2005) and were all mainly focused on TCE. Degradation of TCE to VC or even ethene was often observed in these studies. Investigative methods usually include geochemical and biological approaches while stable isotopes were used in two of the most recent studies (Chartrand et al., 2005; Pierce, 2005). These studies were generally aimed to confirm the occurrence of biodegradation of the chlorinated compounds in these different fractured media by using the above-mentioned methods. In the two studies that used stable isotopes quantification of biodegradation was also performed (Chartrand et al., 2005; Pierce, 2005). Thus, biodegradation of chlorinated compounds seem to be ubiquitous in

various types of fractured bedrocks. However, none of these studies investigated the temporal change of the distribution of contaminants (including chlorinated compounds and substrates such as BTEX and ketones) and the degradation history of the chlorinated compounds in the fractured rocks.

Research in fractured rock aquifers benefits significantly from advanced technologies such as borehole geophysics, hydrophysical logging (Silliman and Robinson, 1989; Williams et al., 2002.), and multilevel monitoring systems (Cherry et al., 2006; Parker et al., 2006b; Taraszki et al., 2002). These technologies significantly enhanced our ability to understand the geology, hydrogeology, groundwater flow, and contaminant distribution in deep fractured rock aquifers. Many of these technologies have been used in the site under investigation of VOCs contamination in this study.

Table 1-1 Field Studies of Degradation of Chlorinated Solvents in Fractured Rock Aquifers

Location	Rock Type	Primary Contaminants	Main Degradation Products	Depth Range of Plume	Age of Contamination	Authors, date	Techniques	Main Conclusion
Near Niagara Falls, New York, US	Dolomite	TCE	cis-DCE, VC, and ethene	To about 20m	-	Yager et al., 1997	Hydrogeological, geochemical, and microbiological methods	Biotransformation of TCE to ethene by naturally occurring microorganisms
-	Basalt	TCE and PCE	-	-	-	Mobarry et al., 1999	Enrichment culturing and PCR-DGGE	Aerobic bacteria that oxidized TCE were most abundant in the core samples. Bacteria diversity in the well was less than in the enrichment culture.
Middle Tennessee, US	Karst deposits	TCE	cis-DCE,VC, ethene, and ethane	6 to 67m	1980	Byl and Williams, 2000	Chemical, biological, and hydrologic methods	Biodegradation of TCE
Oak Ridge, TN, US	Shale	TCE	cis-DCE, VC, and ethene	To 6m	-	Lenczewski et al., 2003	Geochemistry (redox) and microorganism study	Anaerobic degradation (natural attenuation).
-	-	TCE	cis-DCE, VC, and ethene	34 to 40m	-	Chartrand et al., 2005	Biostimulation and bioaugmentation. Stable carbon isotope.	Biodegradation of TCE, cis-DCE, and VC. Quantified biodegradation of cis-DCE and VC.
SSFL, CA, US	Sandstone	TCE	cis-DCE, trans-DCE, and 1,1-DCE	2 to 800m	From 1948	Pierce, 2005	Geochemistry and isotopes	Identified and quantified degradation of TCE and cis-DCE. Origin of major ions.

-: information not found

1.2 Degradation of Chlorinated Compounds

Subsurface degradation of chlorinated compounds in groundwater has been studied for more than 20 years. The degradation pathways for chlorinated ethenes and chlorinated ethanes under various redox conditions are well understood. Although literature is limited on degradation of chlorinated compounds in fractured rock aquifers, the fundamental mechanism should be the same as degradation in granular aquifers (Butler and Barker, 1996; Chapelle, 2001).

Not until the mid-1990's the degradation pathways for biodegradation of chlorinated compounds were understood. These pathways are reductive dechlorination, aerobic oxidation, anaerobic oxidation, and aerobic cometabolism (Chapelle, 2003).

Among all the pathways, reductive dechlorination of chlorinated ethenes is the most important process and has been studied in depth (Figure 1.1). In the process of reductive dechlorination, chlorinated ethenes were used as electron acceptors, not a carbon source and a chlorine atom is replaced with a hydrogen atom. The release of chlorine ions into the solution (groundwater) by reductive dechlorination often leads to the accumulation of chloride. The sequential reductive dechlorination occurs in the order that PCE firstly degrades to TCE; then TCE further degrade to cis-1,2-DCE, trans-1,2-dichloroethene (trans-DCE), and 1,1-dichloroethene (1,1-DCE). Usually cis-DCE is the main product and trans-DCE and 1,1-DCE are the minor products under the influence of biodegradation (Bouwer, 1994). All three isomers of DCE could degrade biotically to VC, which could finally degrade to ethene, the non-chlorinated product. The microbial reductive dechlorination is controlled by subsurface redox conditions, availability of organic substrates to microorganisms, and the availability of certain microorganisms (especially to the degradation of cis-DCE and VC). The redox conditions that are required for each step of microbial reductive dechlorination are described in

detail later. The redox conditions can be created either by anthropogenic pollutants such as ketones and BTEX, which are electron donors, or by natural organic matter in the aquifer. Because the chlorinated ethenes are used as electron donors in the process, there must be a source of carbon serving as the substrates for the microbial growth (Bouwer, 1994). Such source of carbon includes some anthropogenic hydrocarbons such as BTEX and ketones and natural organic matter. Finally, halorespirers, microorganisms that grow using chlorinated ethenes as sole terminal electron acceptors and are capable of high rates of reductive dechlorination, are commonly present, but to date only one, Dehalococcus ethenogenes, has been shown to completely degrade PCE to ethene (Bradley, 2000).

In many cases, reductive dechlorination transforms PCE and TCE to DCEs and VC first and then anaerobic or aerobic oxidation transforms DCEs and VC to carbon dioxide (Chapelle, 2003).

An example of chlorinated ethenes concentrations changing along the flow path is presented, from a study by Chapelle and Bradley (1998) (Figure 1.2). Initially, there were only PCE and TCE in the groundwater near the source. They disappeared rapidly along the flow path to the downgradient and DCE and VC were formed from reductive dechlorination of PCE and TCE. Further downgradient, DCE and VC disappeared due to degradation (probably oxidation) and diffusion. This is a very typical pattern of chlorinated ethenes concentration change along the flow path and has been observed repeatedly in porous media aquifers (Barrio-Lage et al., 1987; Witt et al., 2002). In this pattern, the proportion of degradation products increases along the flow path.

Chlorinated ethenes can also undergo abiotic degradations, but most of the evidences have been obtained in laboratory experiments. In the presence of zero valent iron (Fe(0)), major degradation products from TCE were cis-DCE, 1,1-DCE, VC and trans-DCE as well as ethene and ethane as the dominant gases with minor ones being

methane, propene, propane, 1-butene, and butane (Orth and Gillham, 1996). However, Fe(0) is rarely present in natural systems. Some laboratory experiments showed abiotic degradation of TCE in the presence of natural minerals, such as iron sulfide, clay minerals, pyrite, magnetite, green rust, iron-bearing phyllosilicates, and loamy sand (Pierce, 2005). The major degradation products were found to be acetylene and cis-DCE (Pierce, 2005). Butler and Hayes (1999) found that in the presence of iron sulfide, TCE was transformed to about 71% acetylene and 7% cis-DCE. Thus, the presence of acetylene was used to indicate the occurrence of abiotic degradation of TCE (Pierce, 2005).

Degradation pathways for chlorinated ethanes have also been reported. 1,1,1-TCA is known to degrade both biotically and abiotically (Figure 1.1). In an experiment by Vogel and McCarty (1987), 1,1,1-TCA underwent abiotic degradation to 1,1-DCE and acetic acid through hydrolysis (dehydrochlorination) under anaerobic condition, with a half-life >2.8 years. Anaerobic microorganisms, Methanogens and sulfate reducers, were found to degrade 1,1,1-TCA to 1,1-dichloroethane (1,1-DCA) and further to chloroethane biotically (Grostern and Edwards, 2006). Chloroethane can degrade biotically to ethane or abiotically to ethanol (Vogel and McCarty, 1987). 1,1,1-TCA has been observed to be able to inhibit methanogenesis and reductive dechlorination (Duhamel et al., 2002).

1.2.1 Degradation under Various Redox Conditions

Biodegradation processes are redox processes, so the efficiency of biodegradation largely depends on the ambient redox conditions (Chapelle, 1996). Therefore, redox conditions, if correctly determined, can be used to indicate the degradation potential of certain contaminants.

Basic redox conditions include methanogenic, sulfate reducing, iron reducing, manganese reducing, denitrification, and aerobic conditions, with the methanogenic condition being the most reducing and the aerobic condition being the most oxidative.

Characterization of redox environments in contaminant plumes was reviewed by Christensen et al. (2000). A variety of approaches were proposed to determine redox conditions:

1. redox potential measured in the field,
2. concentration of redox-sensitive compounds in groundwater samples,
3. hydrogen concentrations in groundwater,
4. concentrations of volatile fatty acids,
5. sediment characteristics, and
6. microbial tools.

Among these methods, field measured redox potential (Oxidation Reduction Potential or ORP) and concentration of redox-sensitive species in groundwater samples are commonly used. Redox-sensitive species are those species that participate or are generated in reduction or oxidation processes. Common redox-sensitive species include dissolved ions $SO4^{2-}$, HS^{-}, Fe^{2+}, Mn^{2+}, NH_4^{+}, NO_2^{-}, NO_3^{-}, dissolved gasses CH_4, N_2O and O_2, as well as other components in groundwater (e.g., DOC and organic N) (Christensen et al., 2000).

Among these redox sensitive species, some are most often measured in practice, including dissolved oxygen, nitrate, manganese, iron, sulfate and methane corresponding to aerobic, denitrification, manganese reducing, iron reducing, sulfate reducing, and methanogenic conditions. Usually, a high DO concentration (>1ppm) indicates aerobic conditions (Bjerg et al., 2003), a high manganese concentration indicates manganese reducing conditions, a high iron concentration indicates iron reducing conditions, a low sulfate concentration indicates sulfate reducing conditions, and a high methane concentration indicates methanogenic conditions.

Reductive dechlorination of chlorinated ethenes requires progressively more reducing conditions for the lighter products (Chapelle, 2001). PCE readily undergoes reductive dechlorination to TCE under all anaerobic conditions. Reductive dechlorination of TCE to cis-DCE occurs under at least iron reducing conditions. Reductive dechlorination of cis-DCE to VC requires at least sulfate reducing conditions, but occurs more readily in methanogenic conditions. Reductive dechlorination of VC only happens under methanogenic conditions (Bradley, 2000) (Figure 1.1). As a result of the decreasing potential of reductive dechlorination for the lighter chlorinated ethenes (DCE and VC), reductive dechlorination of chlorinated ethenes is often incomplete in the field and frequently leads to the accumulation of cis-DCE and VC, which are even more toxic (Weaver et al., 1995; Wilson et al., 1995).

The redox conditions for degradation of chlorinated ethanes are not as well-studied as chlorinated ethenes. It seems that abiotic degradation of chlorinated ethanes can happen under various redox conditions. A study showed that biotic degradation of 1,1,1-TCA can happen under aerobic condition, leading to the production of 2,2,2-trichloroethanol, trichloroacetic acid, and dichloroacetic acid (Grostern and Edwards, 2006). Biotic degradation of 1,1,1-TCA under anaerobic condition (which is

normally this case), with the transformation of 1,1,1-TCA to 1,1-DCA and further to chloroethane, usually requires more reducing conditions such as methanogenic and sulfate reducing conditions (Grostern and Edwards, 2006).

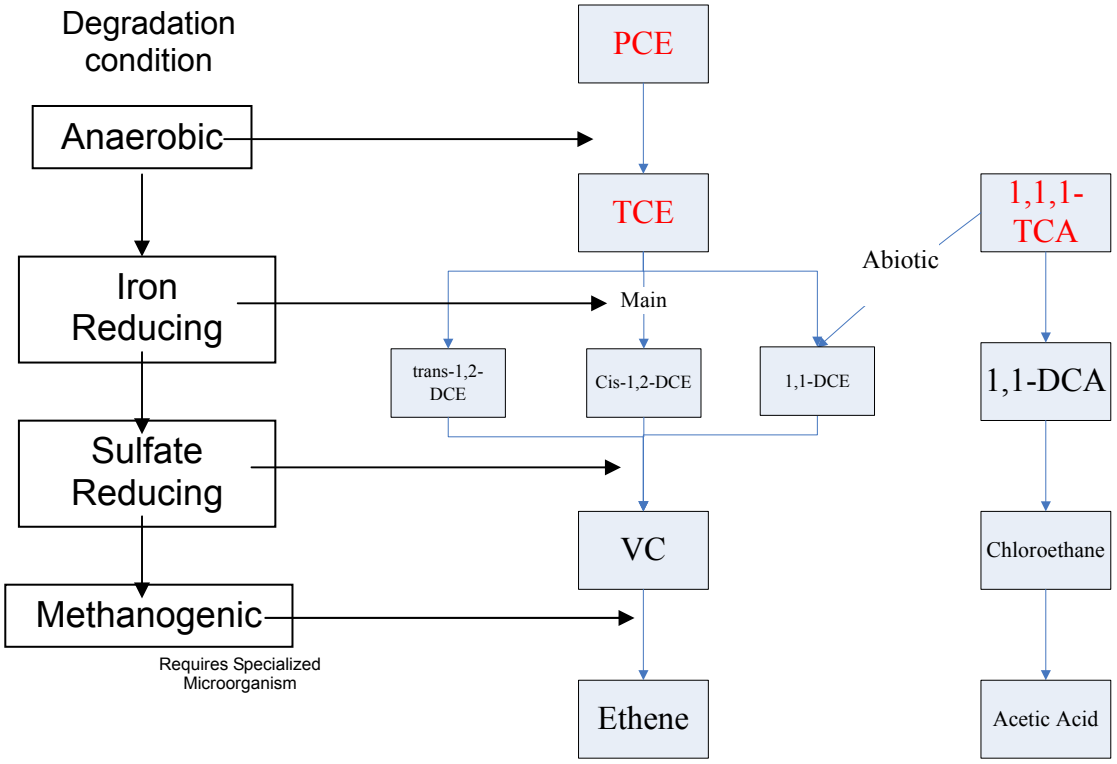


Figure 1.1 Degradation Pathways for Chlorinated Ethenes and Ethanes.

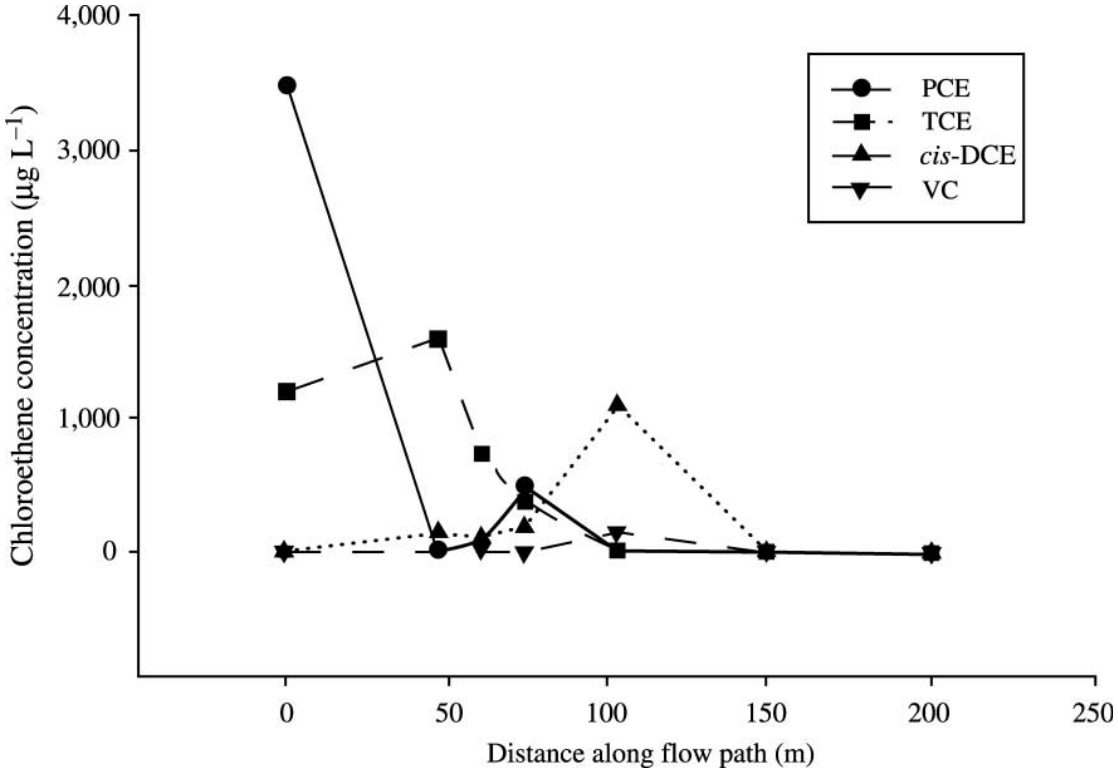


Figure 1.2 Observed Transformation of Chlorinated Ethenes in a Groundwater System. Adopted from Chapelle and Bradley (1998).

1.3 Isotopes for Research on Degradation of Chlorinated Compounds

Many processes can reduce the concentration of organic contaminants in groundwater along the flow path, such as dilution, sorption, dispersion, and degradation. Among all these processes, only degradation can actually reduce the mass of the contaminants in the aquifer. So assessing the extent of degradation of organic contaminants in an aquifer is very important for risk assessment and remediation measures. But it is difficult to differentiate degradation from the other physical processes only based on concentration. A few methods have been proposed to assess degradation processes along the flow path. Among these methods, Compound Specific Isotope Analysis (CSIA) emerged recently and is very promising tool to assess the occurrence and degree of biodegradation of organic compounds..

Definitions and Calculations Common elements such as C, O, H, N, and Cl, that are part of organic compounds, all have several stable isotopes among which one is usually the most abundant. For instance, 98.89% of all carbon on earth consists of the stable carbon isotope ^{12}C and approximately only 1.11% of the stable isotope ^{13}C.

The common way to express the stable isotope ratios of a given element is the delta notation δ [‰] from an international standard. The stable carbon isotope ratio $\delta^{13}C$ is defined as:

$$\delta^{13}C = \left(R_s / R_{std} - 1\right) \times 1000$$

where R_s is the isotope ratio $^{13}C/^{12}C$ of the sample and R_{std} is the isotope ratio $^{13}C/^{12}C$ of the standard. The $^{13}C/^{12}C$ ratio is the ratio between the number of ^{13}C and ^{12}C atoms within the sample. R_{std} is the international standard that all samples are referenced to. The international carbon isotope standard is Peedee Belemnite (PDB, a belemnite fossil from the cretaceous Peedee formation in South Carolina). Stable isotope ratios for

other elements are calculated the same way. The difference in the isotopic ratios is so minor that they are multiplied by a factor of 1000, and referred to as per mil (‰).

Isotopes of one element possess almost identical physical and chemical properties however have a slightly different reactivity during chemical reactions due to the difference in atomic weights. Normally, a heavier isotope is less reactive than a lighter isotope, e.g. a ^{12}C-^{13}C bond is more stable than a ^{12}C-^{12}C bond. This minor difference in reactivity induces what is referred to as isotopic fractionation during reactions, in which heavier isotopes tend to be enriched in the substrates. The isotope fractionation between two compounds (e.g., a substrate and its degradation product) in a reaction can be expressed either with the fractionation factor α or the enrichment factor ε according to the following equations:

$$\alpha = \frac{R_p}{R_r} = \frac{10^{-3}\delta_p + 1}{10^{-3}\delta_r + 1} \text{ and}$$

$$\varepsilon = \left(\frac{R_p}{R_r} - 1\right) \times 1000 = (\alpha - 1) \times 1000 [per\ mil]$$

where the subscripts r and p refer to reactant and product, respectively, R represents the isotope ratio, and δ represents the delta notation. The fractionation factor or enrichment factor, is calculated with the isotope ratios of the substrate and the product in a infinitely short time.

The enrichment factor ε, the initial and final $\delta^{13}C$ values of a substrate, and the residual concentration fraction of the substrate (referred to as f), have the relationship expressed by the Rayleigh equation:

$$\ln\left(\frac{\delta^{13}C+1}{\delta^{13}C_0 + 1}\right) = \varepsilon \ln f$$

where the subscript 0 refers to initial. If three of the four unknowns in the equation are given, the fourth one can be solved.

Applications The prerequisite for using isotope fractionation to differentiate degradation processes from physical processes is that physical processes do not induce significant isotope fractionation. There have been many studies on isotope fractionation during physical processes. Fortunately, a good number of organic compounds including chlorinated compounds satisfy this prerequisite (Meckenstock et al., 2004). Hunkeler et al. (2004) observed that carbon isotope ratios remained relatively constant during dissolution and transport of several chlorinated compounds. Slater et al. (2000) demonstrated that sorption has little effects on the isotope ratios of some organic compounds. Huang et al. (1999) also showed that dissolution and volatilization can't significantly affect the isotope ratios of some organic compounds.

Later, there have been many studies reporting enrichment factors for degradation of various organic compounds. The enrichment factors reported for reductive dechlorination of chlorinated ethenes varied significantly from compound to compound under different conditions (Hunkeler et al., 1999; Bloom et al., 2000; Slater et al., 2001).

Isotope enrichment factors from reductive dechlorination of PCE varied from ε=-2‰ in a microcosm experiment (Hunkeler et al., 1999) to ε=-5.5‰ in a study using a microbial consortium and butyric acid (Slater et al., 2001). Reported carbon isotope enrichment factors for reductive dechlorination of TCE ranged from -2.5‰ to -13.8‰ (Hunkeler et al., 1999; Bloom et al., 2000; Slater et al., 2001), which appeared to be greater than those for PCE. The carbon isotope enrichment factors for reductive dechlorination of cis-DCE and VC were much greater than those for reductive dechlorination of PCE and TCE, ranging from -14.1‰ to -20.4‰ for cis-DCE and -21.5‰ to -31.1‰ for VC (Bloom et al., 2000 ; Slater et al., 2001 ; Hunkeler et al., 2002).

Enrichment factors for reductive dechlorination of trans-DCE and 1,1-DCE are reported to be -30.3‰ and -7.3‰, respectively, by Hunkeler et al. (2002) in microcosm experiments. These values seem to be very different from those reported for cis-DCE.

Studies on isotope fractionation during degradation of chlorinated ethanes are very limited. Carbon isotope enrichment factors for dechlorination of 1,1,2-TCA and 1,2-DCA were determined to be -2.0‰ and -32.1‰, respectively, by Hunkeler et al. (2002). Elsner et al. (2007) reported the enrichment factors of -13.6‰ to -15.8‰ for 1,1,1-TCA reduction by Cr(II), Fe(0), and Cu-plated iron (Cu/Fe) in the laboratory.

An important application of isotopes is to evaluate the degree of degradation of organic contaminants in groundwater. In case of biodegradation of PCE, TCE and cis-DCE, there are two possible scenarios. One is that degradation ceases at cis-DCE without further degradation to VC. In this case the $\delta^{13}C$ value of cis-DCE finally approaches the original $\delta^{13}C$ value of PCE (about -30‰, typically) (Figure 1.3). In the other scenario, degradation of chlorinated ethenes proceeds beyond cis-DCE to VC and the $\delta^{13}C$ value of cis-DCE becomes increasingly enriched, to even positive values (Figure 1.3). Therefore, the $\delta^{13}C$ value of cis-DCE can be used to indicate the significance of its degradation in a sequential degradation starting from PCE.

Most research on the use of isotopes to investigate fate of chlorinated contaminants in the field has been in granular aquifers. Very few have been done in fractured rock aquifers. During a pilot-scale bioaugmentation project, stable carbon isotopes were used to investigate the process of reductive dechlorination in a fractured bedrock plume. Enrichments of ^{13}C in cis-DCE and VC indicated significant dechlorination of these two compounds, disregarding the variable concentration profiles of TCE, cis-DCE, VC and ethene. Quantification of the degradation of cis-DCE and VC was also done using carbon isotopes (Chartrand et al., 2005). In another study in a

fractured sandstone aquifer contaminated mainly with TCE in California, isotopes were used to identify and quantify the degradation of TCE and cis-DCE (Pierce, 2005).

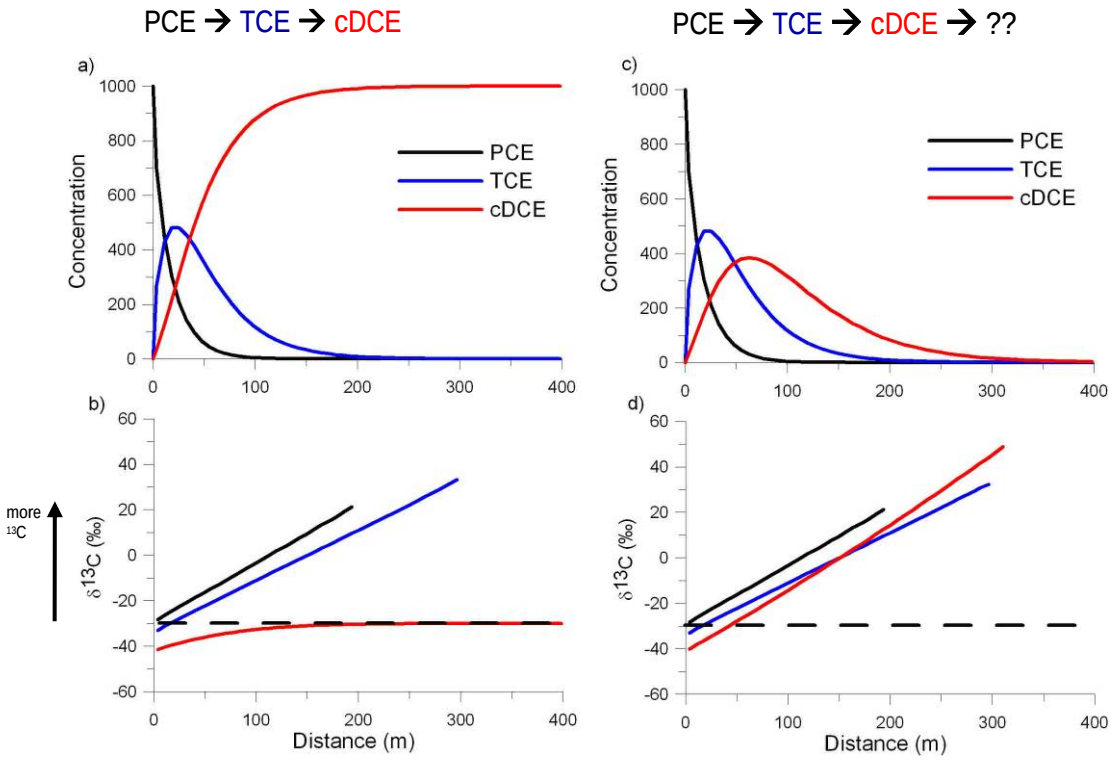


Figure 1.3 Evolution of Concentrations and Carbon Isotopes of PCE, TCE and cis-DCE in Two Scenarios
On the left hand side is a scenario in which degradation of chlorinated ethenes ceases at cis-DCE. On the right hand side is a scenario in which degradation of chlorinated ethenes proceeds beyond cis-DCE.

2 Thesis Objective

The site in South Central Wisconsin has been intensively monitored using conventional monitoring wells and multilevel wells for VOCs including various chlorinated compounds, BTEX, and ketones for more than 15 years. The site has undergone many remediation activities such as soil vapor extraction (SVE), DNAPL pumping, and the operation of a Hydraulic Barrier System. High resolution techniques that are referred to as discrete-fracture network (DFN) investigation approach including detailed rock core sampling techniques have been employed (Parker, 2007). Austin (2005) using a suite of these techniques evaluated the mechanism for which the DNAPL has accumulated in a portion of the Lone Rock Formation (referred to as Layer 5). This study showed that the large storage capacity of the Lone Rock formation for DNAPL in the horizontal fractures and the porous matrix was the main mechanism that explained the accumulation of DNALP in this layer. Meyer (2005) evaluated the retardation of the plume based on the velocity of groundwater flow in the fractures and the actually plume front migration rate, which was obtained from the plume length and the time after DNAPL release. The plume front was found to be retarded by a factor between 4 and 25, with 25 being more likely. This study showed that diffusion-driven contaminant mass transfer from the fractures into the rock matrix contributed strongly to the plume retardation.

The occurrence of biodegradation in the high VOC concentration areas near the DNALP source was documented by Austin (2005). However the extend of VOC biodegradation in the plume has not been properly evaluated and the long term history of biodegradation seemed to be very complex based on preliminary data analysis (see Figure 2.1).

From a plume management perspective, it is important to evaluate the current degree (extent) of degradation to propose more feasible plume management and remediation strategies for the site, such as natural attenuation. From a research point of view, the long term VOC data set collected at this site offers a unique opportunity to evaluate the role of plume management strategies such as DNALP pumping on the current extent and VOC composition of the plume. Therefore, the thesis objectives included: First to have a better understanding of the long term contaminant distribution and degradation history at the site. This objective was accomplished reviewing the VOC historical concentration data collected in wells tapping the most contaminated hydrogeologic units in the bedrock (Layer 5) and in the overburden aquifer (referred as Layer 2) from 1992 to 2006. The second objective aimed to determine the current degree or extent of the degradation of chlorinated compounds, which was accomplished by evaluating the current groundwater redox conditions and a combined use of VOC concentration and carbon isotope analyses.

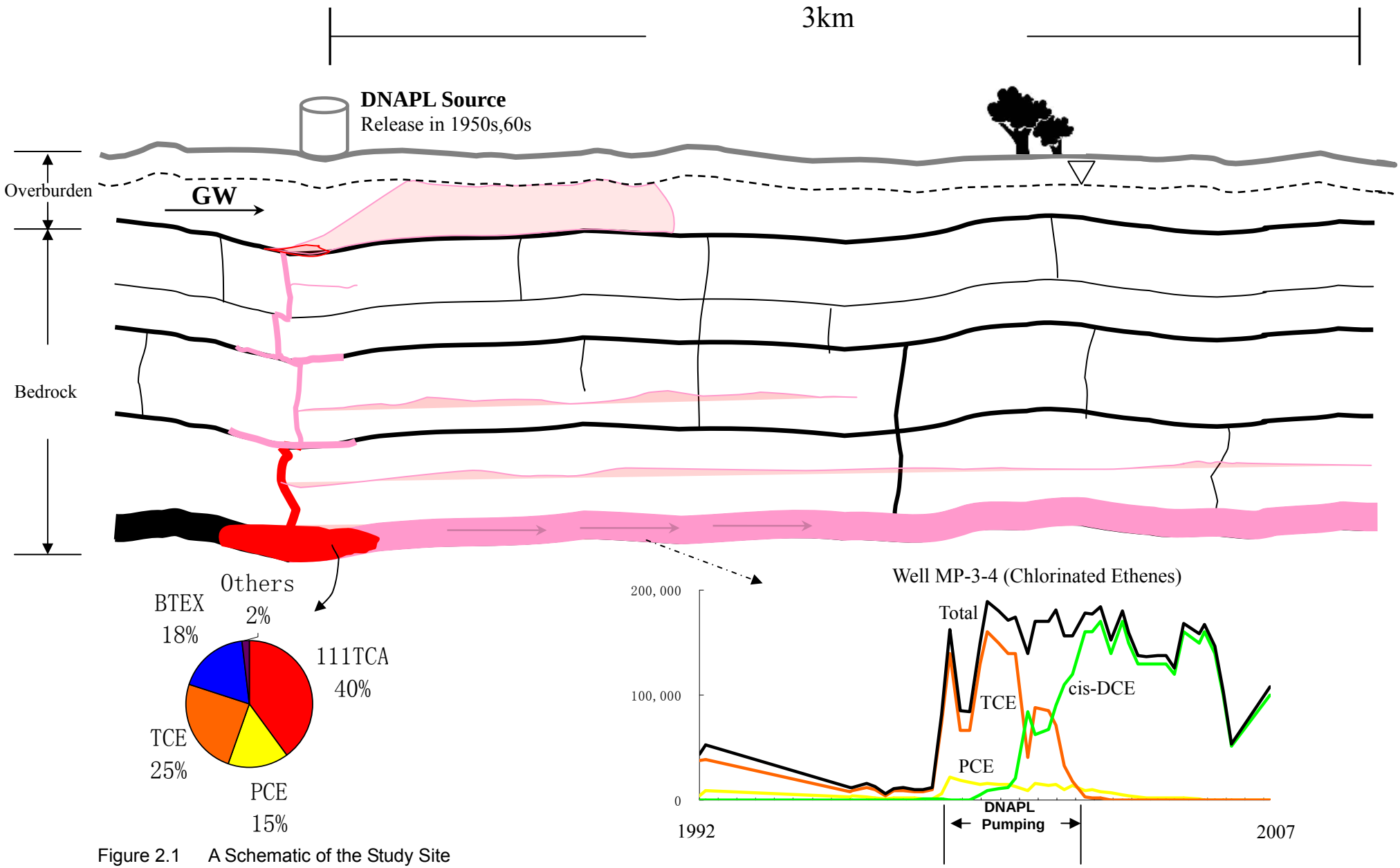


Figure 2.1 A Schematic of the Study Site

3 Site Description

The study site is located in south central Wisconsin, USA, in the village of Cottage Grove which is about 20.5km east of Madison and 111.7km west of Milwaukee (Figure 3.1). The DNAPL source zone (delineated with the red circle in Figure 3.1) is located south of a chemical facility and the majority of the plume is underneath farmlands and wetlands. The current plume has a length about 3km and a width about 2km (delineated with the dashed orange line in Figure 3.1). The study site encompasses a total area of approximately 7.3 km^2. The local relief is about 10.7 m disregarding the local drumlins formed by glaciation and the ground surface elevation range from 262 to 273 m AMSL. The high elevation area is near the contaminant source and the low elevation area covers most of the downgradient plume. Annual precipitation for this area is about 837mm which consists of rainfall mainly in the summer and snowfall in the winter.

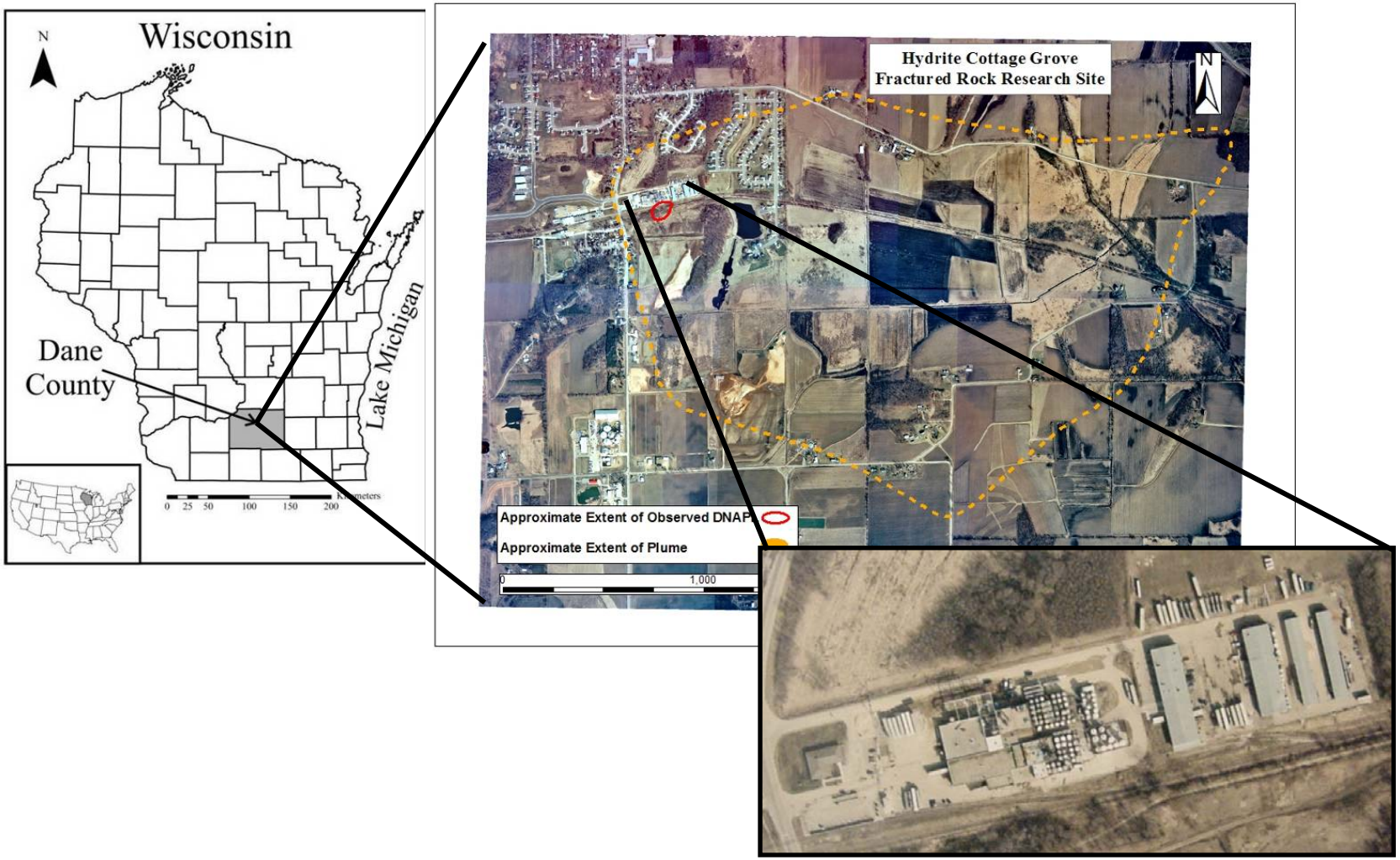


Figure 3.1 Site Location
The site is located in the Dane County in Wisconsin, USA. The air photo of the site on the right includes the extent of the plume (by the orange dash line) and the source zone (by the red circle). The lower air photo shows the chemical facility near the source zone (Courtesy of Jessica Meyer).

3.1 Site History

Before 1950, the site was owned by a farmer's co-op that operated a storage and pumping facility which likely involved petroleum products (HSI GeoTrans, 1998). From the 1950's to the 1960's the site was owned by North Central Chemical Company which was a chemical recycler and distributor (HSI GeoTrans, 1998). The site was used primarily for storage and distribution of waste solvents and chemicals during this time. In 1970, the current owner, Hydrite Chemical Company, bought the property. Presently, Hydrite Chemical, Cottage Grove, Wisconsin Facility is an organic processing, chemical distribution, waste management, and chemical recycling facility. Hydrite Chemical Co. thinks that the subsurface contamination had already occurred before the purchase of the site.

Subsurface contamination was first found in 1982 in the soil during construction of a new building (Hydro-Search Inc. 1989). In 1983, the consulting company, commissioned by the current site owner, started to work on this site. In 1987, bedrock contamination was found and subsequently, two wells were installed for investigation in the bedrock. Free-product DNAPL was first discovered in 1988. In the 1990's, an extensive monitoring network was installed and monitoring began in an effort to find a remediation solution. In 1998, a soil vapor extraction (SVE) in the vadose zone beneath the property of the chemical facility was conducted. An estimated 70,100 kg of contaminants was removed by the SVE (HSI GeoTrans, 1999). An additional 30,000 kg of contaminants was estimated to be destroyed by oxidation with air brought into the vadose zone by aeration (HSI GeoTrans, 1999). From 1999 to 2002, large-scale DNAPL extraction in the source zone was performed by the consultants. About 34,000 L DNAPL was pumped from the bedrock during this period of time. It was estimated that there were still 72,680 L DNAPL remaining in the source zone in the bedrock (GeoTrans Inc., 2003).

A Hydraulic Barrier System, including four extraction wells P-128, P-130, P-145, and P-164 in the middle of the plume pumping contaminated groundwater from the most contaminated layer, has been under operation since October 2003.

University of Waterloo researchers have studied the site since August 2003 focusing on investigations of flow regime and contaminant distribution in the bedrock. Two graduate students finished their theses on this site in 2005. The thesis by Austin (2005) mainly explained the reason for DNAPL accumulation in the upper part of Lone Rock Formation and the thesis by Meyer (2005) investigated the groundwater flow and retardation of the large plume in the most contaminated section of the bedrock about 50m below ground surface.

Currently, there are more than 300 permanent groundwater monitoring wells, DNAPL recovery wells, piezometers, and multilevel systems (Figure 3.2) ranging from depths of 9 m bgs to more than 152 m bgs (based on Meyer, 2005). About 1/4 of the monitoring locations were screened in the most contaminated layer, referred to as Layer 5. Most of these monitoring locations have been sampled quarterly or semi-annually for analyses of concentration of VOCs. Contaminants detected in groundwater from the site include volatile organic compounds (VOCs), semi-volatile organic compounds, heavy metals, and PCBs. Semi-volatile organic compounds, heavy metals, and PCBs were only occasionally detected and the resulting low concentrations were considered to be not of concern (HSI GeoTrans, 1998). Thus, research has been focused on VOCs. The composition of VOCs has changed over time. However, the basic components in the groundwater are always halogenated compounds, aromatics, and ketones. The DNAPL has all the above components except ketones.

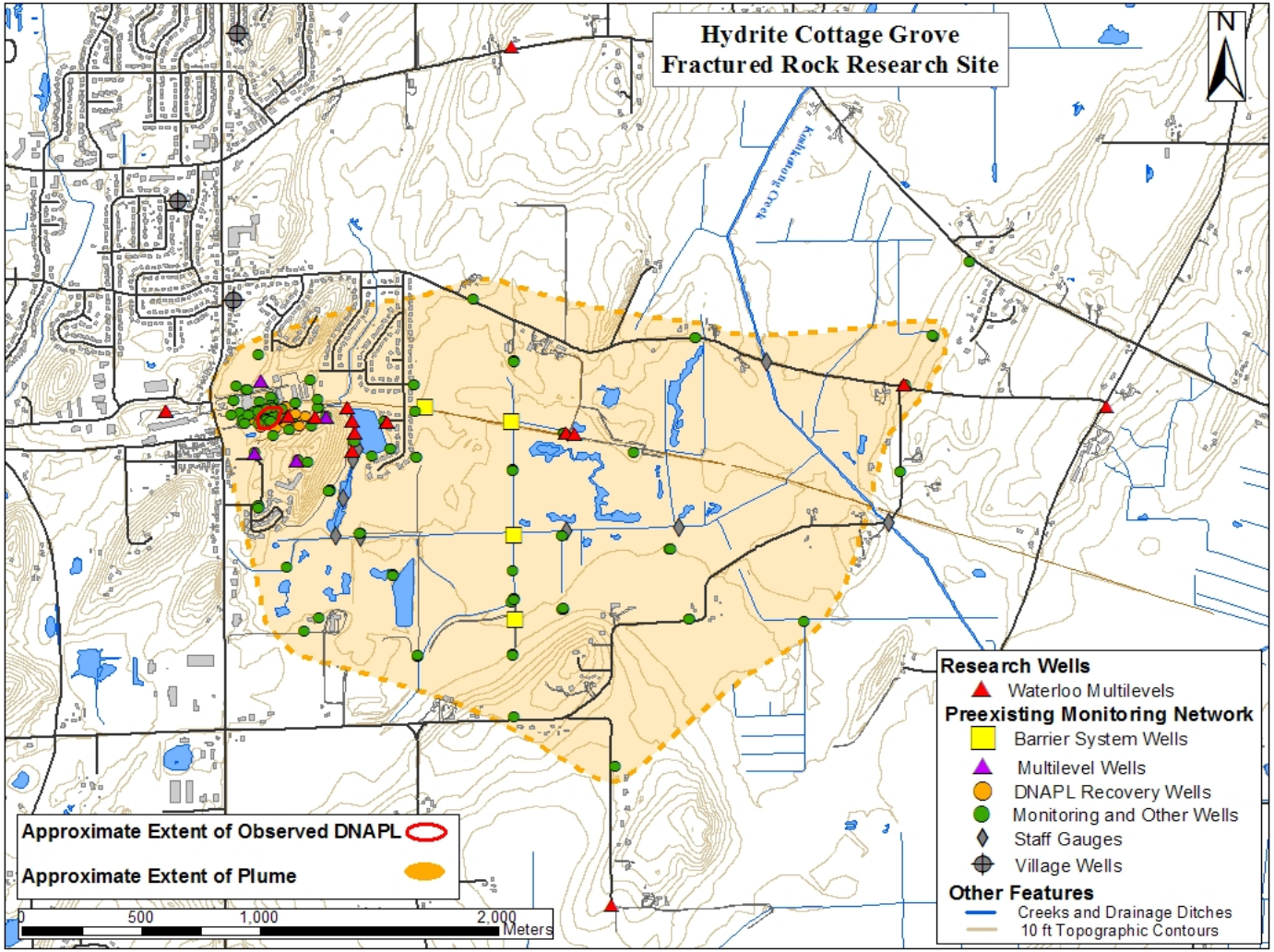


Figure 3.2 Monitoring Network of the Site

There are currently more than 300 permanent groundwater monitoring wells, DNAPL recovery wells, piezometers, and multilevel systems at the site. Multilevel systems installed by University of Waterloo are shown in red triangles. DNAPL zone and plume extent are also shown in the figure (Courtesy of Jessica Meyer).

3.2 Geology

Meyer (2005) and Austin (2005) describe the site specific geology in detail. Most importantly, the sequence of stratigraphic units at the site from the top to the bottom includes glacial overburden, St. Peter Formation, Prairie du Chien Group, Jordan Formation, St. Lawrence Formation, Lone Rock Formation, Mazomanie Formation, Wonewoc Formation, Eau Claire Formation, and Mt. Simon Formation (Figure 3.3).

Within the overburden and the Lone Rock Formation is where most of the contamination is located. The overburden is a glacial till (24-27m thick), which consists of fine to medium grained and yellowish-brown to brownish yellow silty sand. Five to thirty percent of the overburden is pebbles, cobbles and boulders. At the bottom of the overburden there is 0-3.3 m of silty clay till or fill.

The Lone Rock Formation, which is about 45m below ground surface, contains three major sublithologies: a flat pebble conglomerate in a glauconite matrix, a laminated quartz-glauconite feldspathic sandstone, and a bioturbated quartz-glauconite sandsonte (Sutherland, 1986). Note that glauconite is iron rich.

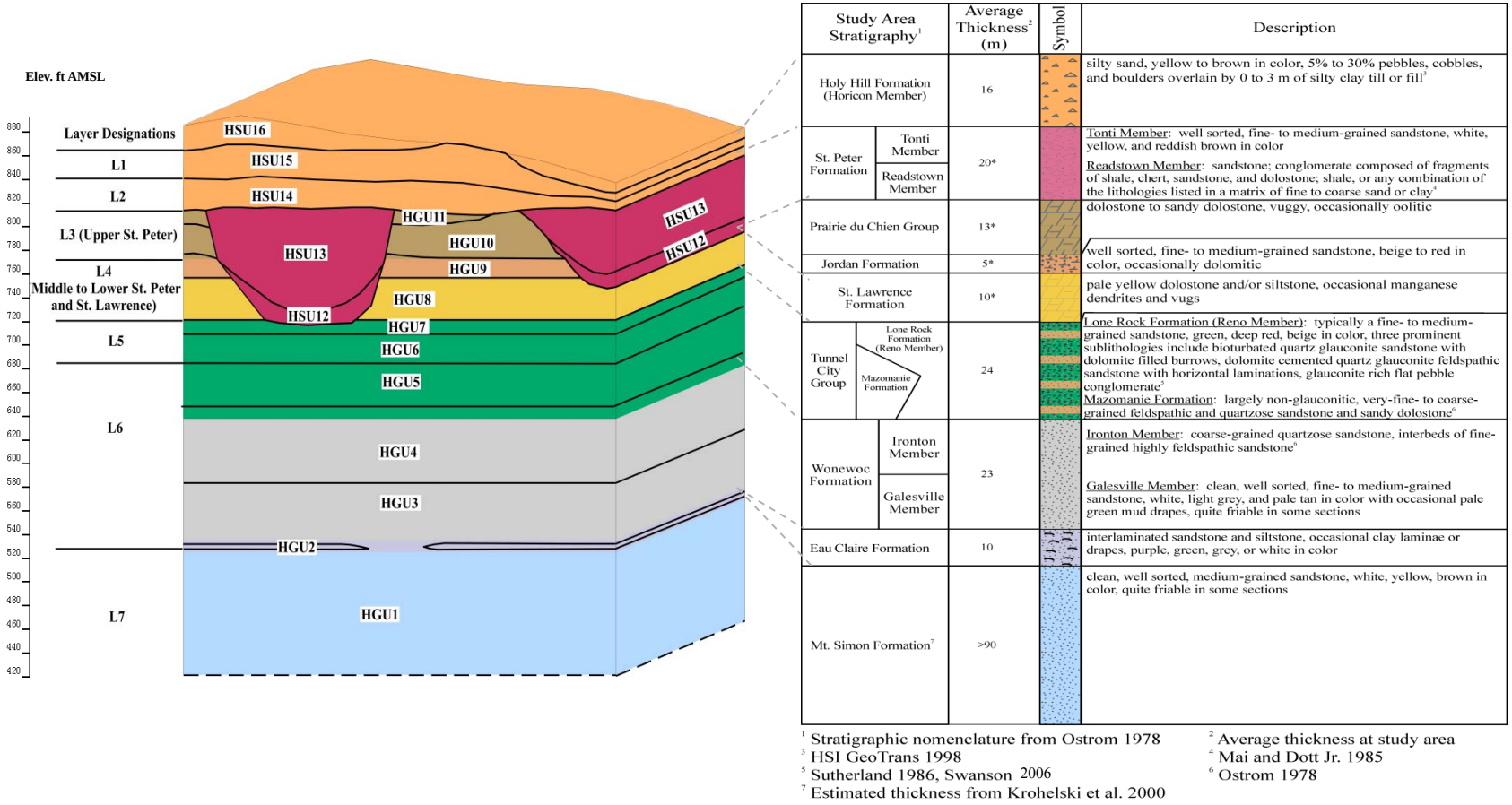


Figure 3.3 Lithology and Hydrogeologic Layer Designation Systems

This figure is a schematic representation of the lithology and hydrogeologic layer system of the site. Detailed stratigraphy from the top to the bottom generally includes glacial overburden, St. Peter Formation, Prairie du Chien Group, Jordan Formation, St. Lawrence Formation, Lone Rock Formation, Mazomanie Formation, Wonewoc Formation, Eau Claire Formation, and Mt. Simon Formation. Three designation systems are shown by the labels. The GeoTrans designation system uses the notation L. (Courtesy of Jessica Meyer)

3.3 Hydrogeology

The hydrogeology of the site has been studied in depth by the University of Waterloo graduate students. Austin (2005) focused on the hydrogeology in the source zone which might have an impact on the distribution of DNAPL. Meyer (2005) studied the groundwater flow pattern in the whole plume area by using groundwater head profiles and detailed rock core sampling.

The recharge zone and discharge zone at the site correspond to the zone near the source (the red area) and the low topography zone in the plume area (the yellow area), respectively (Figure 3.4).

Local groundwater recharge and discharge are active not only in the overburden but also in part of the bedrock. This can be indicated from the head profiles of three multilevel wells in the bedrock (Meyer, 2005) (Figure 3.5). The three multilevel wells are: MP-6 located upgradient to the source zone to the west, MP-5 located in the middle of the plume, and MP-8 located at the front of the plume to the east. In MP-6 hydraulic gradient was observed to be always downward, which indicated groundwater recharge from the ground surface into the bedrock in area near the source zone. In MP-5 and MP-8 upward hydraulic gradient was observed above the upper Tunnel City Group, indicating groundwater discharge from the bedrock to the ground surface in the downgradient area. Furthermore, groundwater gradient below the upper part of the Tunnel City Group is not affected by local recharge indicating the presence of regional groundwater flow system in the deeper bedrock.

The vertical hydraulic gradients are large in these profiles, however actual vertical groundwater flow seems to be minor based on the head profiles of the multilevel wells (Figure 3.5). Significant changes of hydraulic head coincided very well with the transition of hydrogeologic layers, indicating much less vertical permeabilities at these

boundaries. Groundwater flow across these boundaries is expected to be insignificant due to these very low vertical permeabilities. The distinct hydraulic heads in different layers also indicated little hydraulic connections between these layers. Hydraulic head was almost constant within each hydrogeologic unit, indicating minor vertical flow inside a unit. Therefore, the conceptual model of groundwater flow at this site based on the head profiles is that horizontal flow within each hydrostratigraphic unit seems to be dominant.

Currently, there are several hydrostratigraphic designation systems (shown by the labels in Figure 3.5). The hydrostratigraphic system, labeled as "L", introduced by the consulting company, is based mainly on geological stratigraphy. This system divides the overburden into two layers, with Layer 1 above and Layer 2 below the water table. It designates the upper St. Peter Formation as Layer 3, middle to lower St. Peter and St. Lawrence Formations as Layer 4 and the Lone Rock Formation which is the upper part of the Tunnel City Group as Layer 5. Layer 6 and Layer 7 are underneath and are almost uncontaminated. Layer 5 is where most of the DNAPL has accumulated and thus the groundwater is most contaminated. Layer 2 has also been found to be highly contaminated likely due to accumulation of DNAPL above the bedrock. This hydrostratigraphic designation system would be used throughout the study.

New hydrostratigraphic designation systems, labeled as "HSU" or "HGU" (Figure 3.5), were suggested by students of University of Waterloo based on extensive geological, hydrogeological, and geophysical logs (Meyer, 2005). The new systems are more accurate and detailed. However, the designation system introduce by the consultants is sufficient when only contamination in Layer 5 and Layer 2 is studied.

The direction of groundwater flow at this site is mainly from west to the east. The contour plot of the potentiometric surface of Layer 5 in February, 2001 illustrated the expected groundwater flow direction at the site (Figure 3.6). The contour plot of the

potentiometric surface of Layer 5 during the September 2007 sampling round (Figure 3.7) covered a smaller area of the site. Two sink points at wells P-116 and P-129 were observed. These two sink points were likely caused by groundwater extraction in wells P-145 and P-128 nearby, which were part of the Hydraulic Barrier System started after October 2003.

The Layer 5 plume within the Lone Rock Formation emanates from the source zone towards the east, generally following the groundwater hydraulic gradient. However, it seems to be wider than expected.

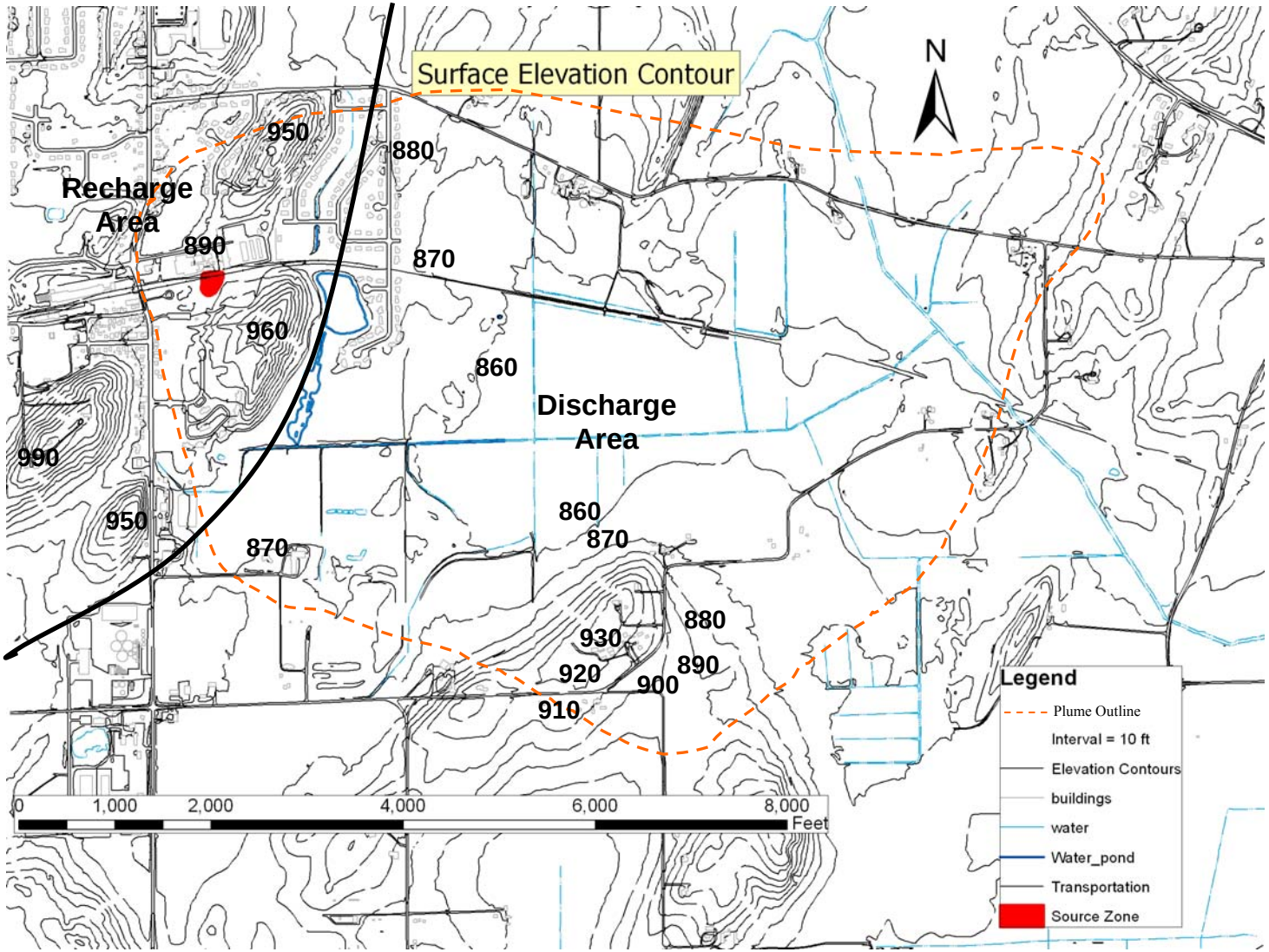


Figure 3.4 Surface Elevation Contour and Delineation of the Recharge and Discharge Areas
Elevation is high to the west near the source zone (the red area) and low in the downgradient plume area, corresponding to the recharge area and discharge area, respectively. The plume extent is shown by the dash line.

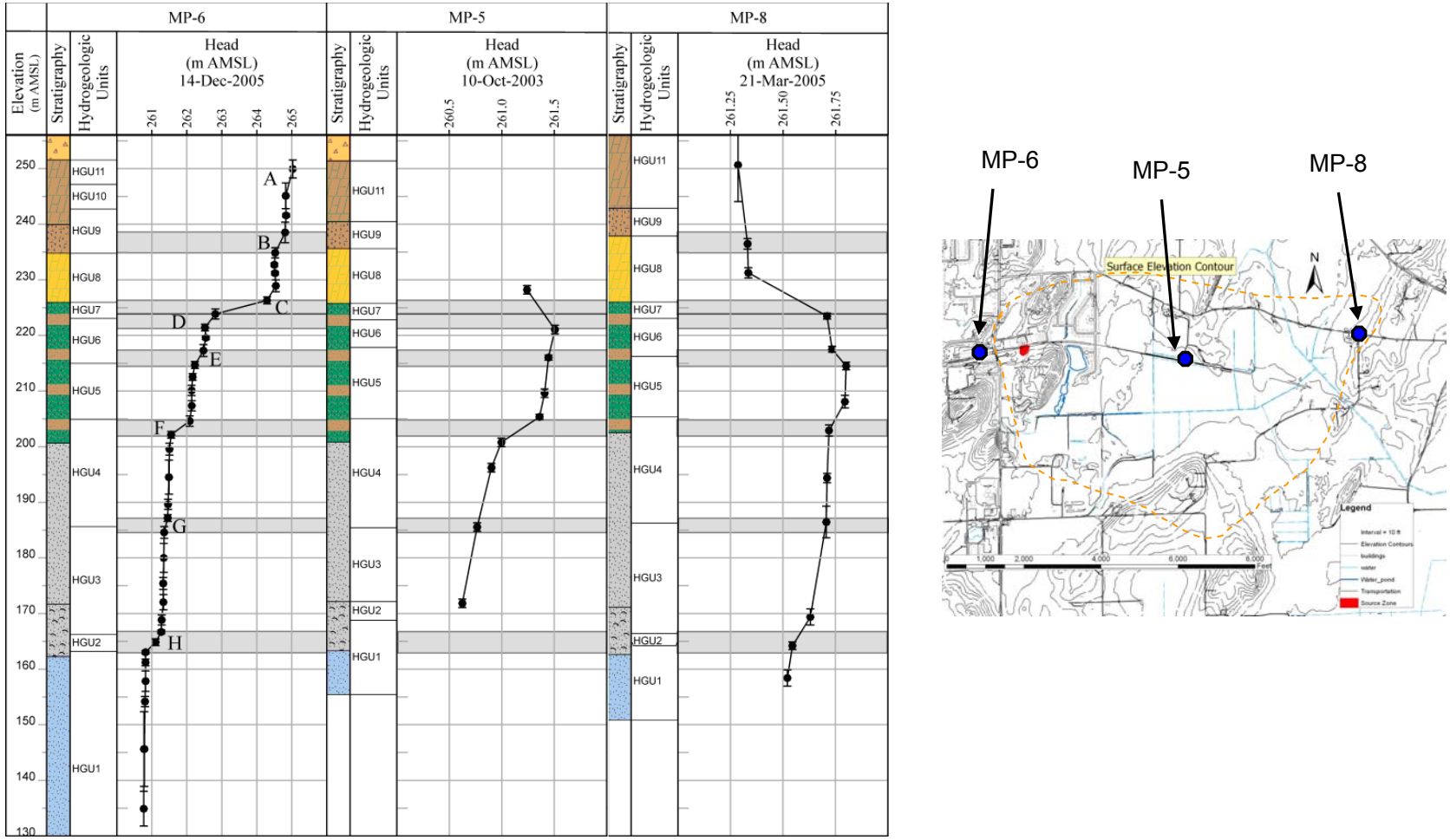


Figure 3.5 Head Profiles of Multilevel Wells MP-6, MP-5, and MP-8

MP-6, MP-5 and MP-8 are located at the upgradient, middle, and front of the plume (delineated earlier), respectively. Sharp change of head between hydrogeologic layers and constant head within each layer might indicate the dominance of horizontal flow. (Figure from Meyer, 2005)

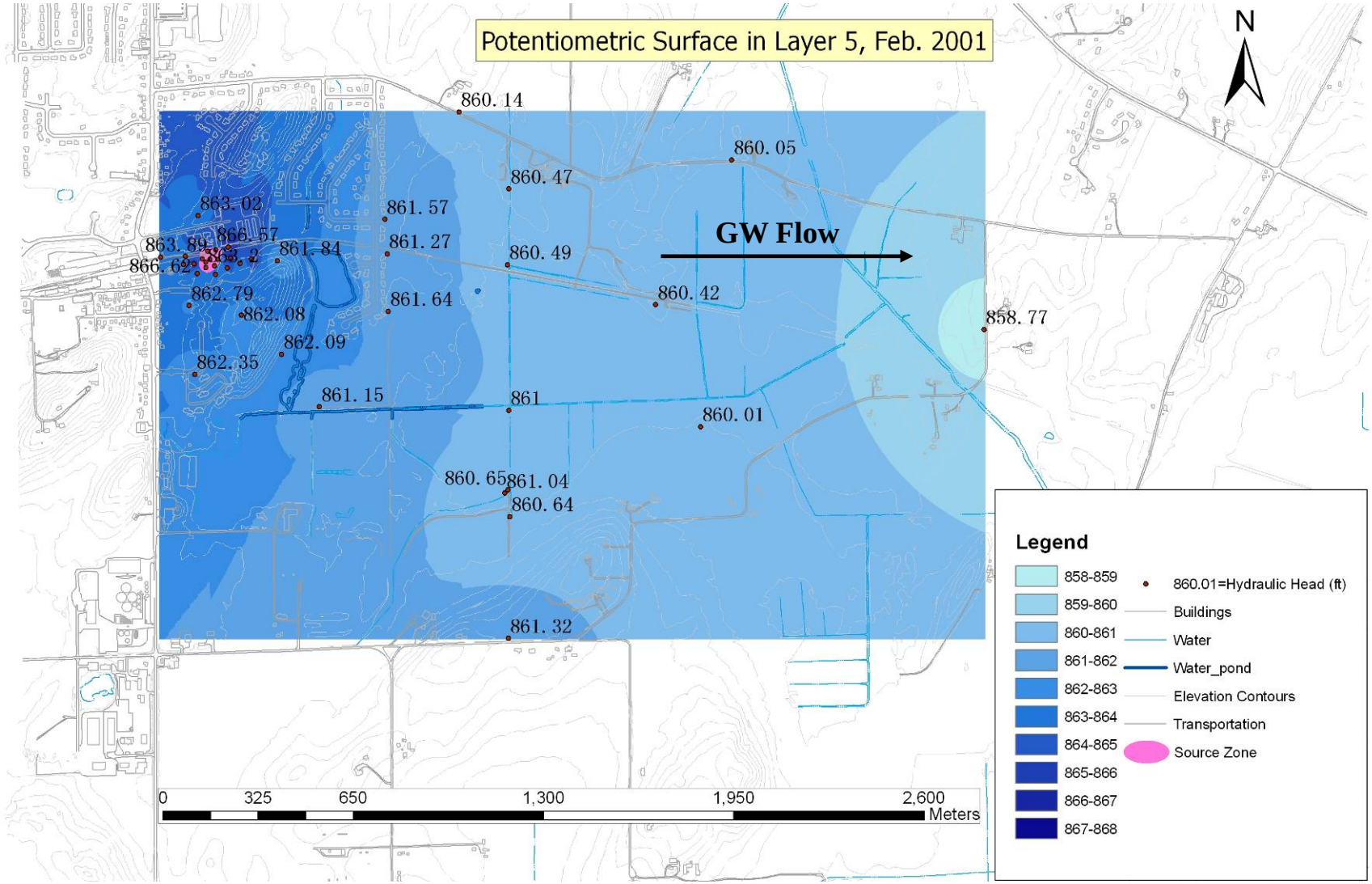


Figure 3.6 Contour of Potentiometric Surface of Layer 5 in Feb 2001
Darker blue represents higher hydraulic head. Groundwater flow is determined to be mainly from west to the east.

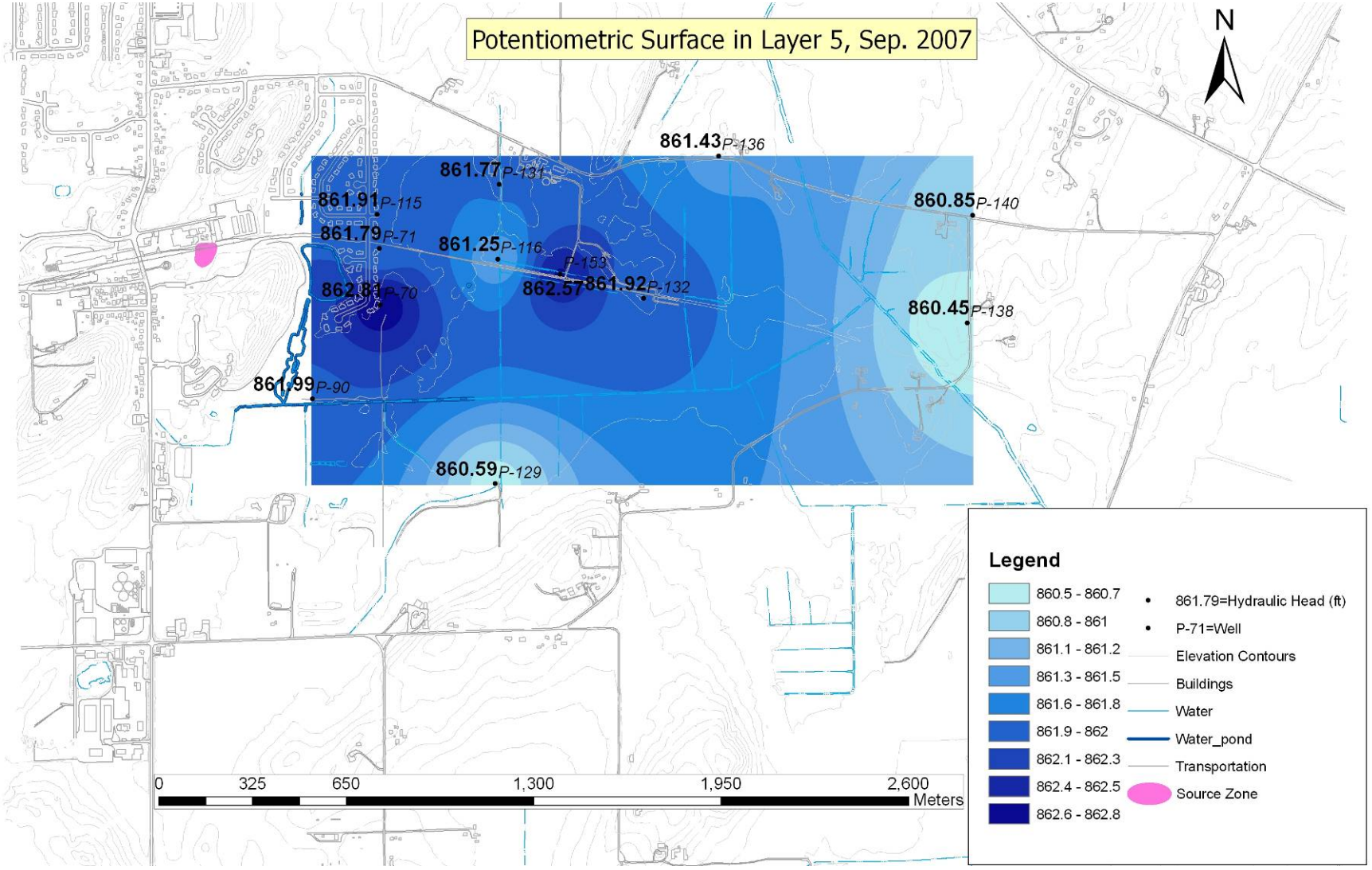


Figure 3.7 Contour of Potentiometric Surface of Layer 5 in Sep 2007

Darker blue represents higher hydraulic head. The contour shows an eastward gradient and a southward gradient. But the heads in the wells P-116 and P-129 are likely significantly influenced by the groundwater extraction in wells P-145 and P-128, which are just nearby P-116 and P-129, respectivley.

3.4 DNAPL Distribution and Composition

The DNAPL spill at the site is thought to have occurred in the 1950's and 1960's when the site was owned by the previous owner - the chemical distribution and recycling plant (HSI GeoTrans, 1998). The DNAPL accumulated in the Lone Rock Formation without migrating to even lower formations probably due to DNAPL head dissipation into the spacious horizontal fractures and porous matrix (Austin, 2005).

Austin (2005) analyzed many DNAPL samples, with the latest analysis in October, 2004 and the DNAPL composition was found to be quite constant spatially and temporally. Thus only the composition obtained from one well RW-111 in the October 2004 sampling round is shown (Figure 3.8). The DNAPL was mainly composed of chlorinated compounds, including 1,1,1-TCA (39.97%), PCE (15.31%), and TCE (24.65%) and very small amounts of (less than 1%) of cis-DCE, 1,1-DCE, and 1,1-DCA. There were also significant amounts (19%) of benzene, toluene, ethyl-benzene, xylenes (BTEX).

1,1,1-TCA, PCE, and TCE are precursors on the top of degradation pathways. They are electron acceptors in the process of microbial reductive dechlorination. BTEX serve as electron donors to create reducing redox conditions in the aquifer, which are suitable for microbial reductive dechlorination. Ketones, which are even stronger electron donors than BTEX, were found in the groundwater near the source zone, but not in the DNAPL because ketones dissolve much faster than the other components. With both electron acceptors and electron donors in the DNAPL and groundwater, it is expected that significant biodegradation of the chlorinated compounds occur in the aquifer. The composition of the DNAPL will serve as the benchmark for the original contaminant composition.

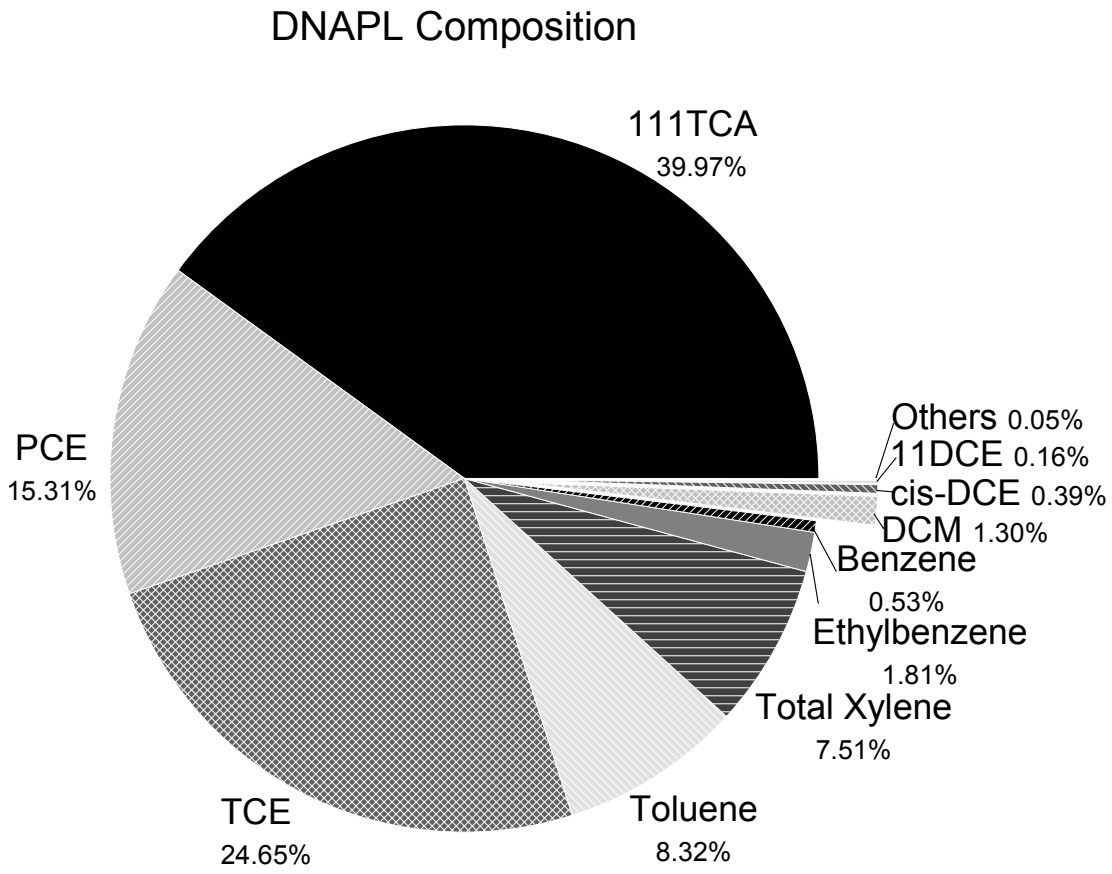


Figure 3.8 Composition of the DNAPL
This figure shows the composition of the DNAPL collected from RW-111, in Oct 2004. (Data from Austin, 2005).

3.5 Groundwater Contamination in Different Layers

Recent groundwater contamination in different layers is evaluated using the data set collected in June 2006, which covered most of the monitoring wells. The concentrations of total VOCs in Layer 1 ranged from 11 μg/L to 552 μg/L, which were the lowest among all the layers (Figure 3.9). Layer 3 and Layer 4 had concentrations ranging from 5.5 to 20,901 μg/L and 3.5 to 3,279 μg/L, respectively (Figure 3.9). Except the highest concentration, Layer 3 generally had relatively low concentrations below 1,300 μg/L. Layer 6 had been found to be relatively clean with the exception of one well (P-38) which had an unusually high concentration, 958,100 μg/L (Figure 3.9). This high concentration was likely linked to the fact this well is located within the DNAPL zone just below Layer 5.

Layer 2 had a highest VOCs concentration of 293,860 μg/L, which was much higher than the concentrations in the overlying Layer 1 and underlying Layer 3 (Figure 3.9). This pattern has been observed from each data set collected at the site. Layer 5 had VOCs concentrations ranging from 7.2 μg/L to 179,920 μg/L and many wells far away from the source zone still had concentrations over 1,000 μg/L (Figure 3.9), exhibiting much more extensive contamination. Thus, Layer 5 is the focus of the study.

A well nest including wells P-53, MP-3-1, MP-3-2, MP-3-4, and MP-3-5 in Layer 2, 3, 4, 5, and 6, respectively, near the source was analyzed to evaluate the vertical distribution of the contaminants (Figure 3.9). Layer 2 through Layer 6 had concentrations of 293,860 μg/L, 20,901 μg/L, 297 μg/L, 156,890 μg/L, and 14 μg/L, respectively. This pattern of much higher concentrations in Layer 2 and Layer 5 has always been observed during the whole sampling period (also shown by the data from March 2002 in Figure 3.10).The high concentration of VOCs within Layer 2 can be explained by the

accumulation of DNAPL on top of the bedrock where this overburden layer is located (Figure 3.10). The high concentration within Layer 5 was caused by DNAPL accumulation within this layer, as described in section 3.4.

Layer 5 and Layer 2 are the two most contaminated layers and they are distinct geological environments: Layer 5 is a bedrock aquifer about 50m below ground surface while Layer 2 is an overburden aquifer just on top of the bedrock. This study focuses on Layer 5 though Layer 2 is often used for comparison.

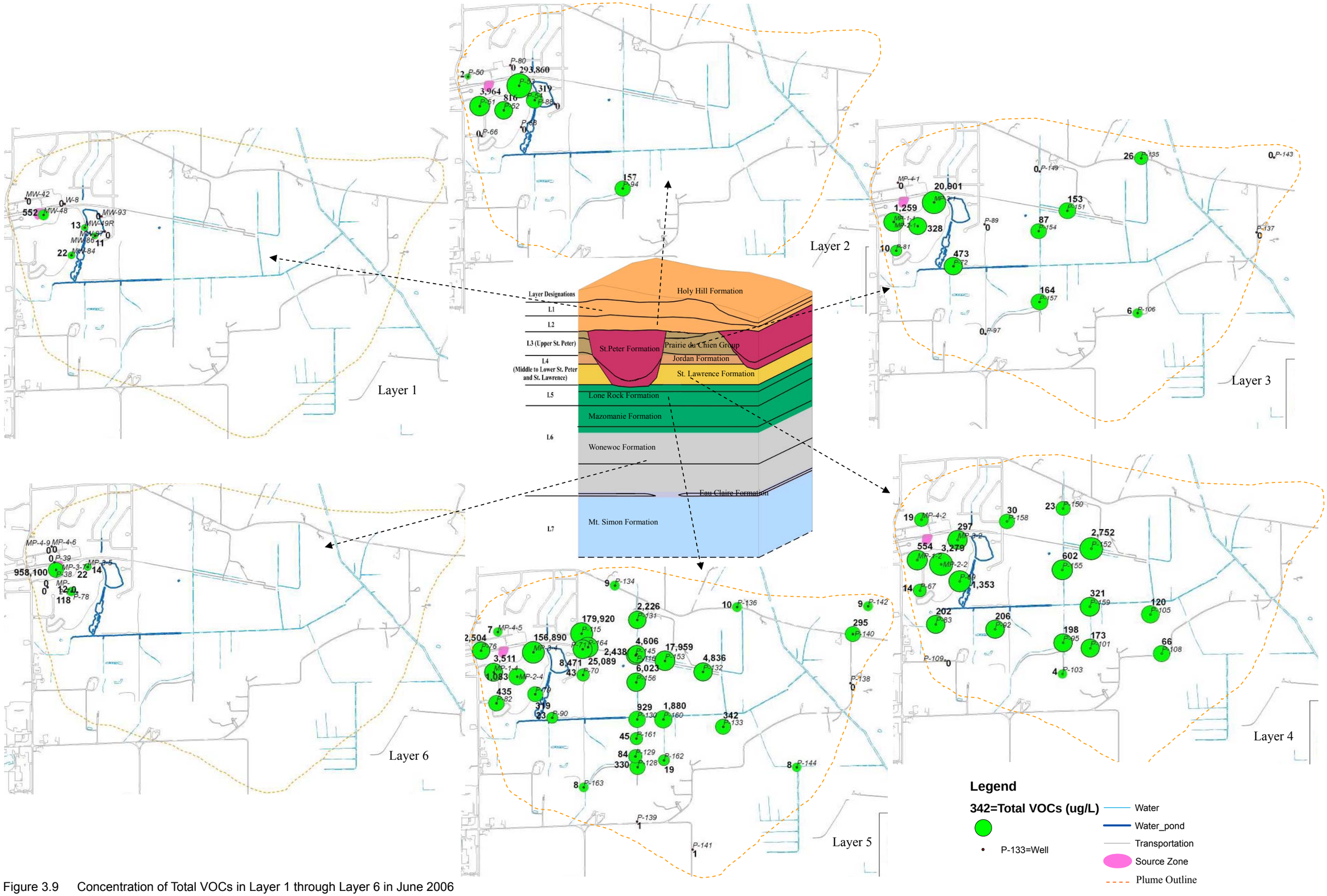
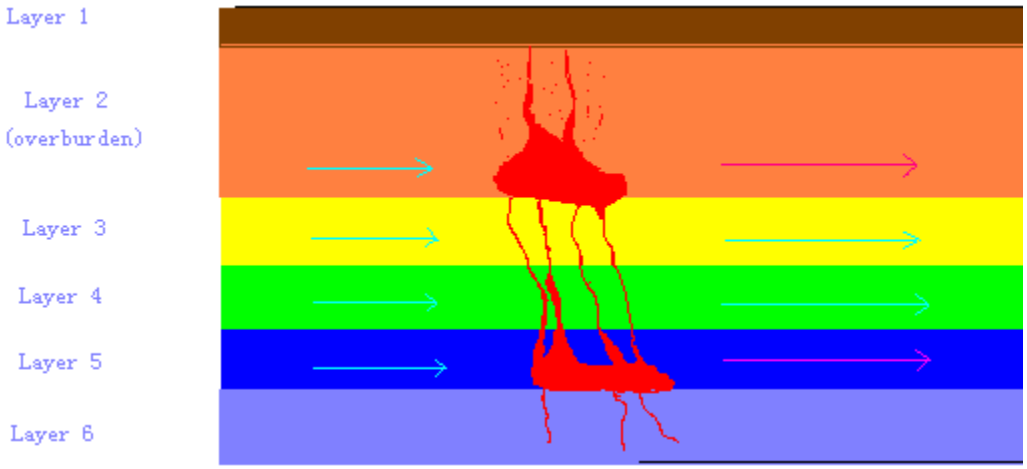


Figure 3.9 Concentration of Total VOCs in Layer 1 through Layer 6 in June 2006

DNAPL Accumulation in
Layer 2 and Layer 5



Concentrations and composition of chlorinated ethenes at the location of MP-3-4, Mar 2002

	VOCs concentration (ug/L)	Composition
Layer 2	243279	Ketones, cis-DCE and VC
Layer 3	436.3	cis-DCE, a little VC and 1,1-DCE
Layer 4	304.6	VC and a little cis-DCE
Layer 5	801800	cis-DCE, TCE and PCE
Layer 6	58.1	--

Figure 3.10 DNAPL in the overburden and bedrock and Concentration and Composition of VOCs in Different Layers
On the left hand side is a schematic representation of the DNAPL accumulation at the site. On the left hand side is a table showing VOC concentrations and compositions at one location in Layer 2 through Layer 6 in March 2002. The high concentration of VOCs within Layer 2 can be explained by the accumulation of DNAPL on top of the bedrock where this overburden layer is located. The high concentration within Layer 5 was caused by DANPL accumulation within this layer.

4 Materials and Methods

4.1 Sampling

4.1.1 Sampling Locations

Based on VOCs data collected in previous years, forty-one sampling locations (Table 4-1) were selected for this study. The selection was based on the criteria to cover the whole range of degradation phases and redox environments in the entire plume area.

The 41 sampling locations consisted of 27 GeoTrans wells which were installed by the consulting company and 14 ports of UW multilevel wells (MP-6 and MP-8) which were installed by the University of Waterloo (Table 4-1). The locations of these wells within each layer (except Layer 6, which has only few sampling locations) are shown in Figure 4.1 to Figure 4.3, and the majority of the wells were selected within Layer 5 (Figure 4.3). Note that wells P-145 and P-164 in Layer 5 are extraction wells in the Hydraulic Barrier System. The layer number for each selected sampling location is listed in Table 4-2.

4.1.2 Sampling Methods

Sampling was completed between the 5th and 15th of September 2007. The most common wells are the conventional wells which have dedicated pumps installed inside (Figure 4.4). An electronic dedicated-pump-controller was connected to the well through an air tube and a water tube, with a flow-through-cell meter (QED MP20) connected to the end. The controller was used to control the pressure of the pump, thus to adjust the pumping time and recovering time to maintain a low flow sampling condition. In each cycle, the wells were pumped for a certain time and left to recover for a certain time after which groundwater parameters (temperature, pH, DO, ORP, and EC) were measured. This process was repeated until the groundwater parameters stabilized, which was considered to be when the last 3 readings were within 5 percent of one another. Once the groundwater parameters had stabilized, groundwater samples were collected.

GeoTrans staff Todd Thomson, who was from the consulting company to perform routine groundwater sampling, conducted all these procedures before the collection of samples. After that, three 40ml vials of groundwater samples for VOCs analysis were collected by Todd Thomson first, preserved by hydrochloric acid. Five 40ml glass vials of groundwater samples preserved with 4 drops of 10N sodium hydroxide in the lab were collected by Ziheng Miao and Paulo Lima from the University of Waterloo. Headspace in the vials was eliminated by the following steps: 1) slowly fill the vial until a reverse meniscus formed above the top of the vial. 2) screwed on the cap, inverted, and tapped the sample vial to check for presence of air bubbles. 3) if air bubbles were present due to collection technique, steps 1 and 2 were repeated. If bubbles were present due to degassing of samples water, it was documented on the Chain of Custody and the Field Log Book. One 250ml polyethylene bottle, without any preservative, was filled with groundwater for anions analysis and another one preserved with 2.5ml of 35 percent

nitric acid was filled through a 0.45 μm filter for cations analysis. All the vials and bottles collected by Ziheng Miao and Paulo Lima were stored in coolers packed with ices and shipped back to the University of Waterloo, where they were kept in fridges until analyzed.

Westbay™ Multilevel (Schlumberger) systems (MP-3 and MP-6) were constructed with no tubing inside and utilize a downhole tool to access each port (Figure 4.5 and Figure 4.6). To sample these wells, firstly a mast and a sampler winch were set up to the well and cables were connected to them. A sampler probe and 4 sample containers were then connected to the cables. An electronic controller was connected to the probe. After that, surface function checks were performed as follows: 1. the arm was released and the shoe was activated, 2. the valve was closed, 3. vacuum was checked, 4. the valve was opened, 5. air was evacuated from the stainless steel sample containers to 2-4 psi with a vacuum pump, 6. the valve was closed, and finally 7. the shoe and the arm were retreated. The probe and containers were then lower to the well to a certain depth by releasing the cables. The desired port was found by measuring the depth (length of the cables in the well) and listening to the beeps that sounded when the probe was lowered past the magnetic collars located at each port. The sampler probe was then landed to the desired port by releasing the arm, when the zone pressure inside the MP casing was recorded from the controller. The shoe was then activated to attach the sampler probe to the monitoring port, when the pressure of the formation was recorded. By opening the valve on the probe, groundwater flushed into the containers by vacuum and the final zone pressure was recorded when the pressure in the containers approached the pressure in the formation. The sampling valve was closed, the shoe was retracted and the pressure in the MP casing was recorded again. The arm was retracted and the sampler probe and containers were slowly raised to ground surface. The sampler probe was disconnected

from the sample containers and excess pressure was vented from the last container. Groundwater was transferred from the stainless steel sample containers to sampling containers, similarly to the procedures for sampling in the conventional wells. Groundwater was also transferred to a small container for measurements of electrical conductivity (EC) and pH. Equipment decontamination was conducted after sampling for each port.

Well MP-8 was a Waterloo^{TM} Multilevel (Solinst) system in which each sampling port had a dedicated tube to the ground surface (Figure 4.7 and Figure 4.8). A peristaltic pump was used to pump groundwater through these tubes. Groundwater parameters were not measured due to the potential of groundwater degassing caused by pumping. Three well volumes were purged before sampling of each port. Groundwater flow was controlled so as to be as low and as continuous as possible to ensure high sampling quality. The procedures to collect samples for different analyses and to store the samples were the same as above.

Well MW-49R was a conventional well without a dedicated pump installed inside. A bailer was used to collect the groundwater samples. Before sampling, at least three well volumes were purged from the well. The bailer was slowly lowered down to the bottom of the well and pulled up manually. Groundwater samples were then collected from the bottom of the bailer by gently displacing the ball in the bailer to form slow flow. Groundwater parameters except DO and ORP were measured. Procedures to collect and store the samples were the same as above.

Sampling and storing methods for each analysis are summarized in Table 4-3.

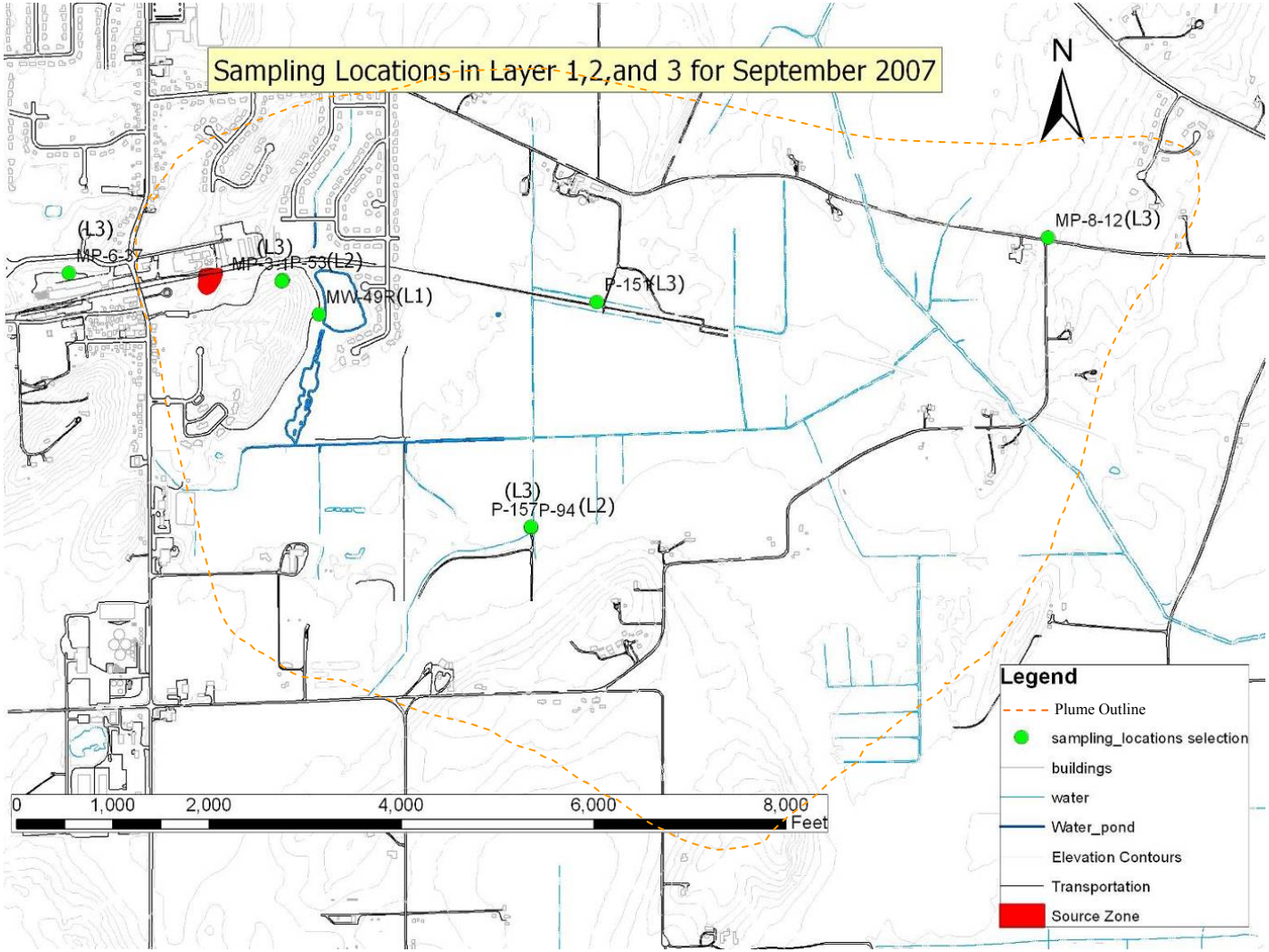


Figure 4.1 Sampling Locations in Layer 1, 2, and 3 for the September 2007 Sampling Round
A few wells were sampled in Layer 1, 2, and 3. The layer numbers are labeled beside each well, e.g. L1 means the well is screened in Layer 1.

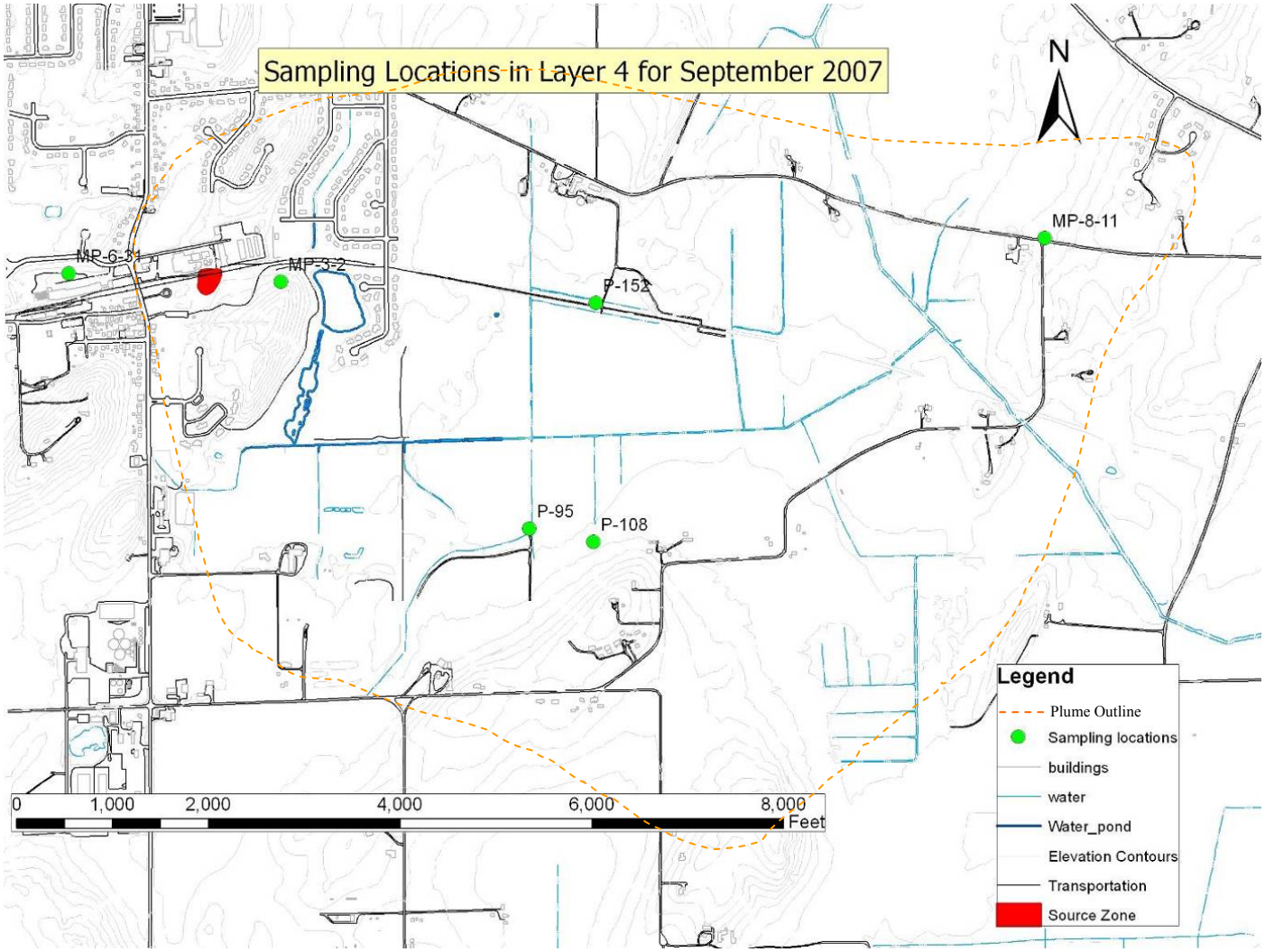


Figure 4.2 Sampling Locations in Layer 4 for the September 2007 Sampling Round
Six locations were sampled in Layer 4. The locations were selected to cover the entire plume area and to have some well nests.

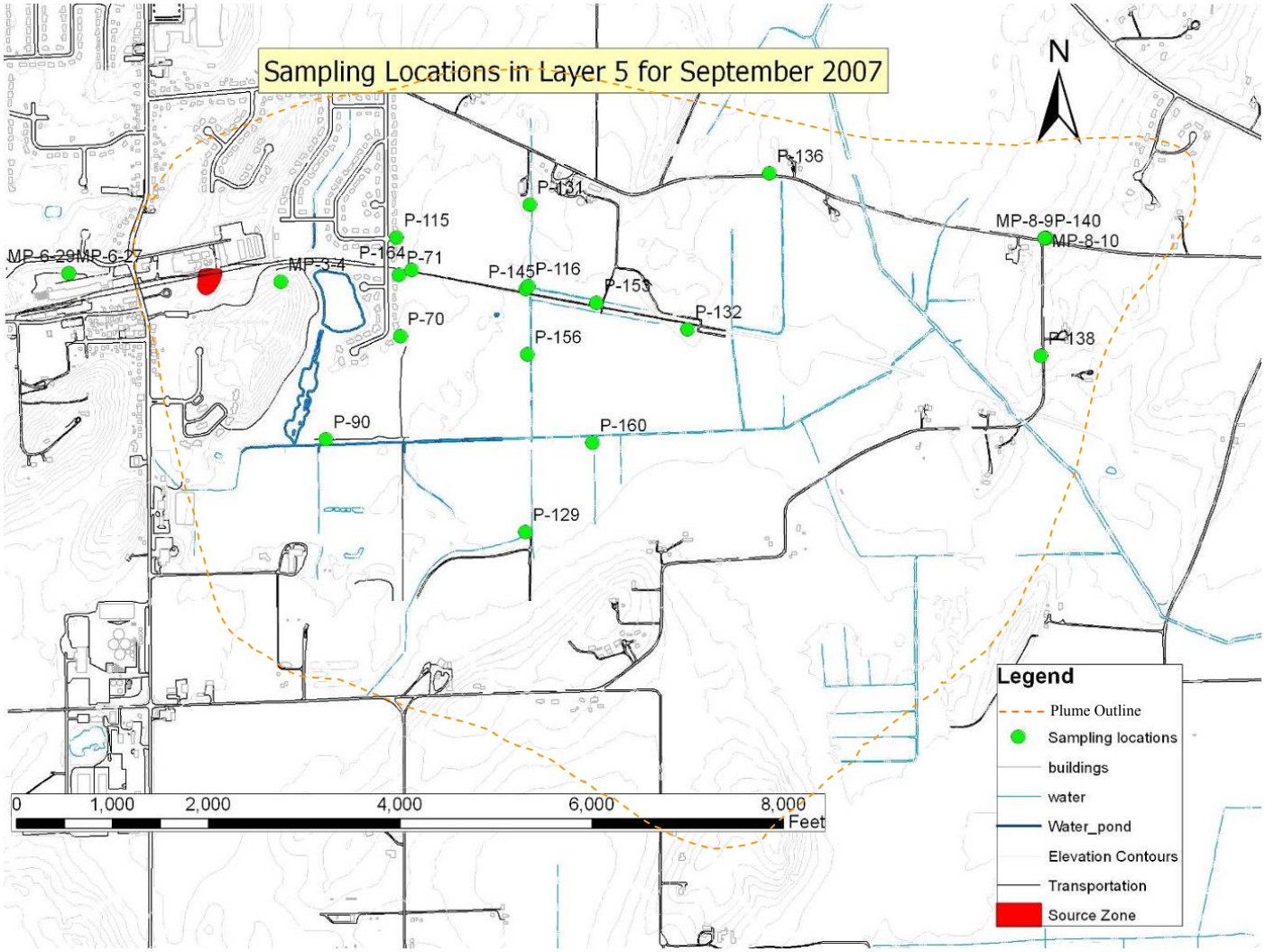


Figure 4.3 Sampling Locations in Layer 5 for the September 2007 Sampling Round
Most of the sampling locations were selected within Layer 5. The locations were selected to cover the whole range of degradation phases, redox environments, and the entire plume area.

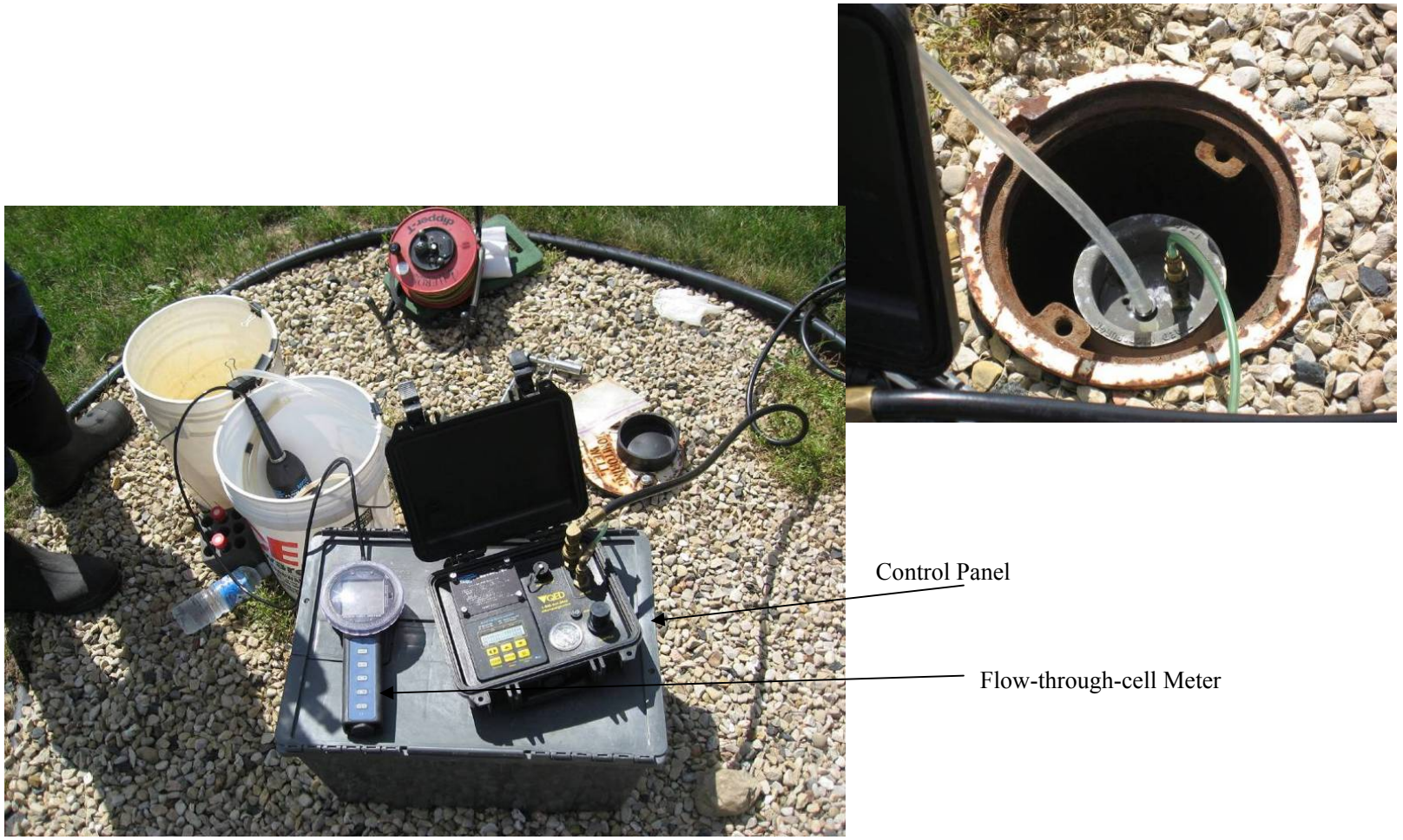


Figure 4.4 Sampling in a Conventional Well

Conventional wells are equipped with dedicated pumps inside. Sampling needs a control panel and a flow-through-cell meter. The control panel is connected to the well through an air tube and a water tube and is used to control the pumping and recovering time to maintain low flow sampling condition. The flow-through-cell meter is used to measure groundwater parameters and indicate the timing for sampling.

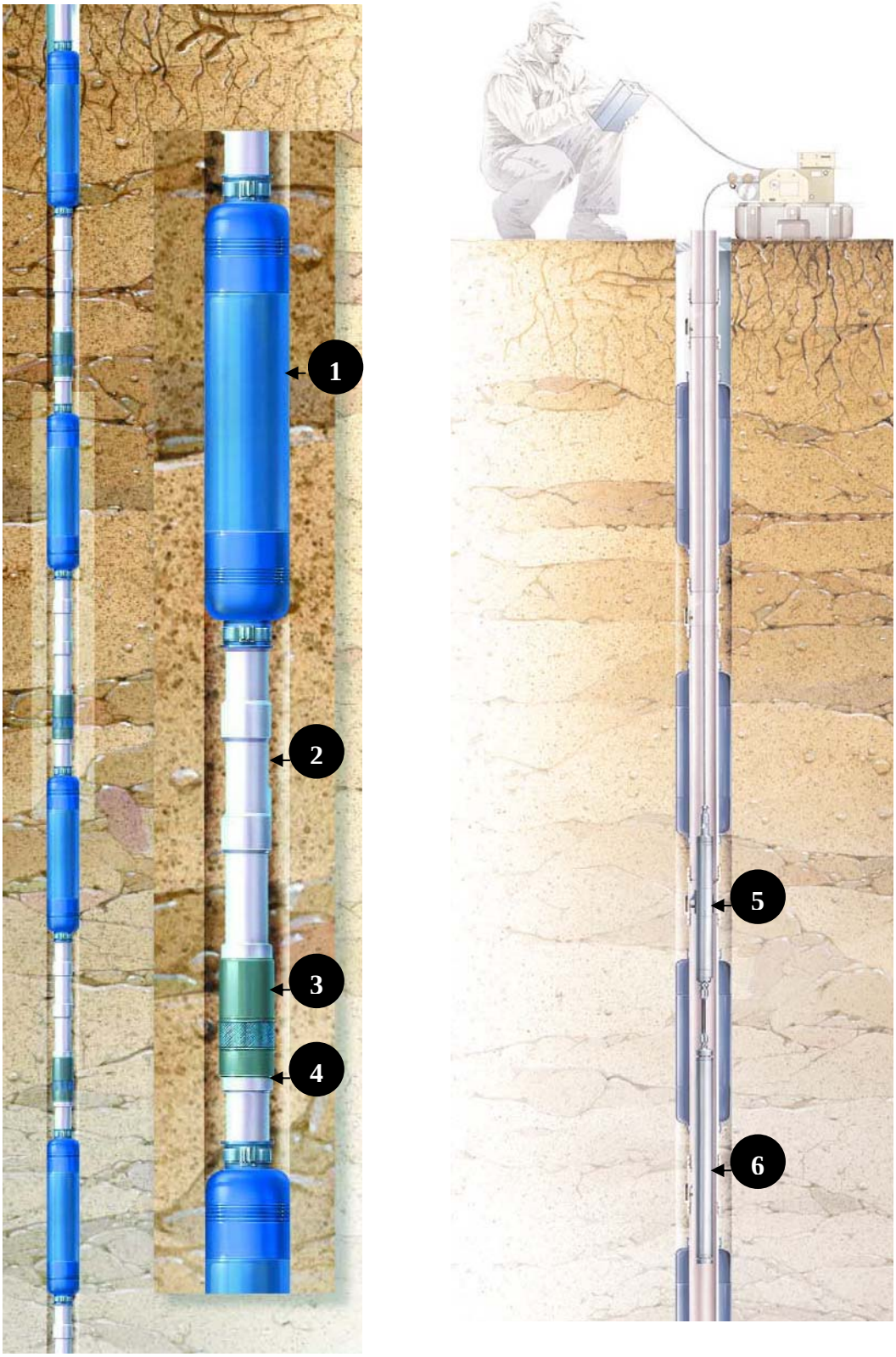


Figure 4.5 Westbay^{TM} Multilevel Well Completion
The Westbay System is a multilevel monitoring technology that allows testing of hydraulic conductivity, monitoring of fluid pressure and collection of fluid samples from multiple zones within a single borehole. The labels on the figure refer to: (1) MP packer, (2) MP Measurement Port, (3) MP Pumping Port, (4) Sealed Connections, (5) Sampler Probe, and (6) Sample Container. (From Schlumberger, 2006)

Figure 4.6 Sampling in Westbay Multilevel System MP-3
Well MP-3 was a typical Westbay Multilevel System. Sampler probe and sample containers were connected to a cable, which was rolled on a mast and a sampler winch. A control meter connected to the sampler probe was used to control the function of the probe and display parameters such as pressure. The sampler probe and sample containers were lowered to the desired port and the containers were filled with groundwater. When they were retreated to the ground surface, samples were collected from the containers.

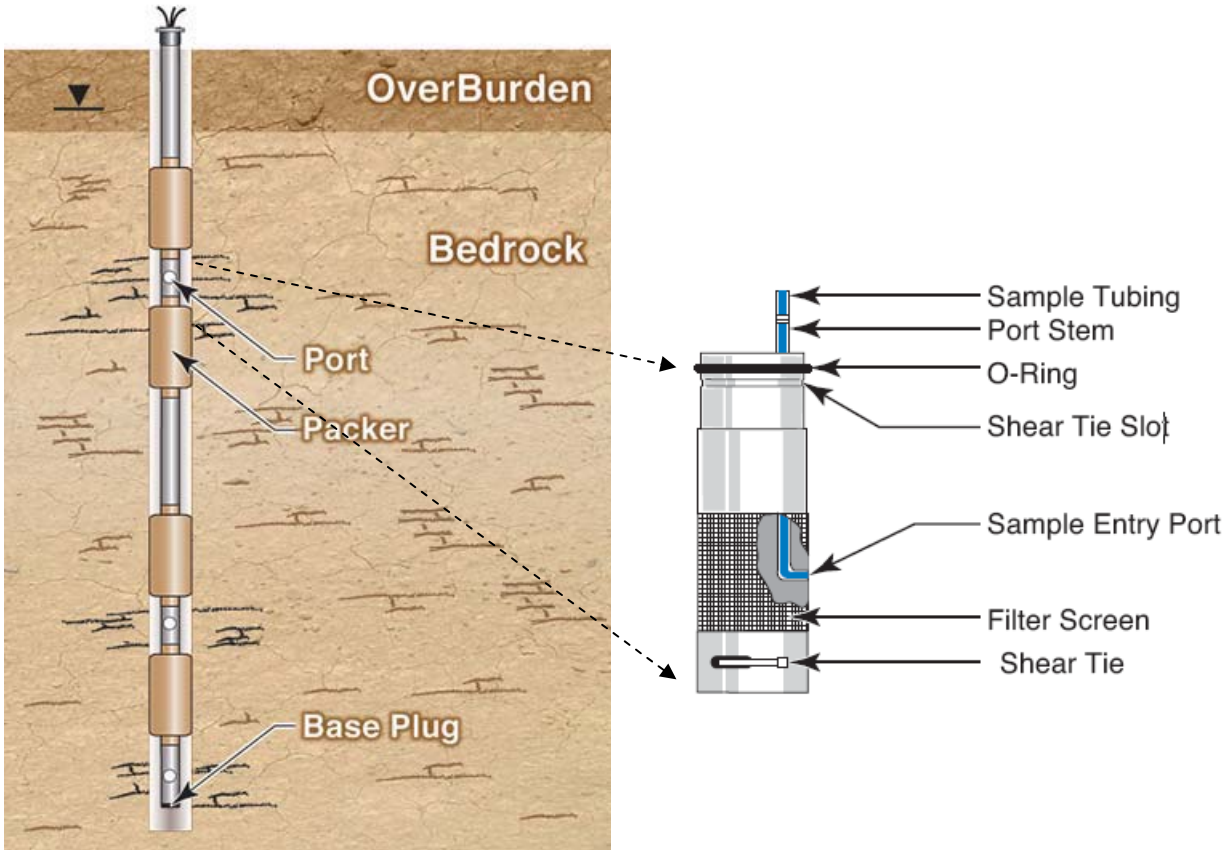


Figure 4.7 Waterloo^{TM} Multilevel System
The Waterloo Multilevel System (Solinst, Canada) is used to obtain groundwater samples, hydraulic head measurements and permeability measurements from many discretely isolated zones in a single borehole. Each sampling port has a dedicated tube to the ground surface. (From Solinst, 2005)

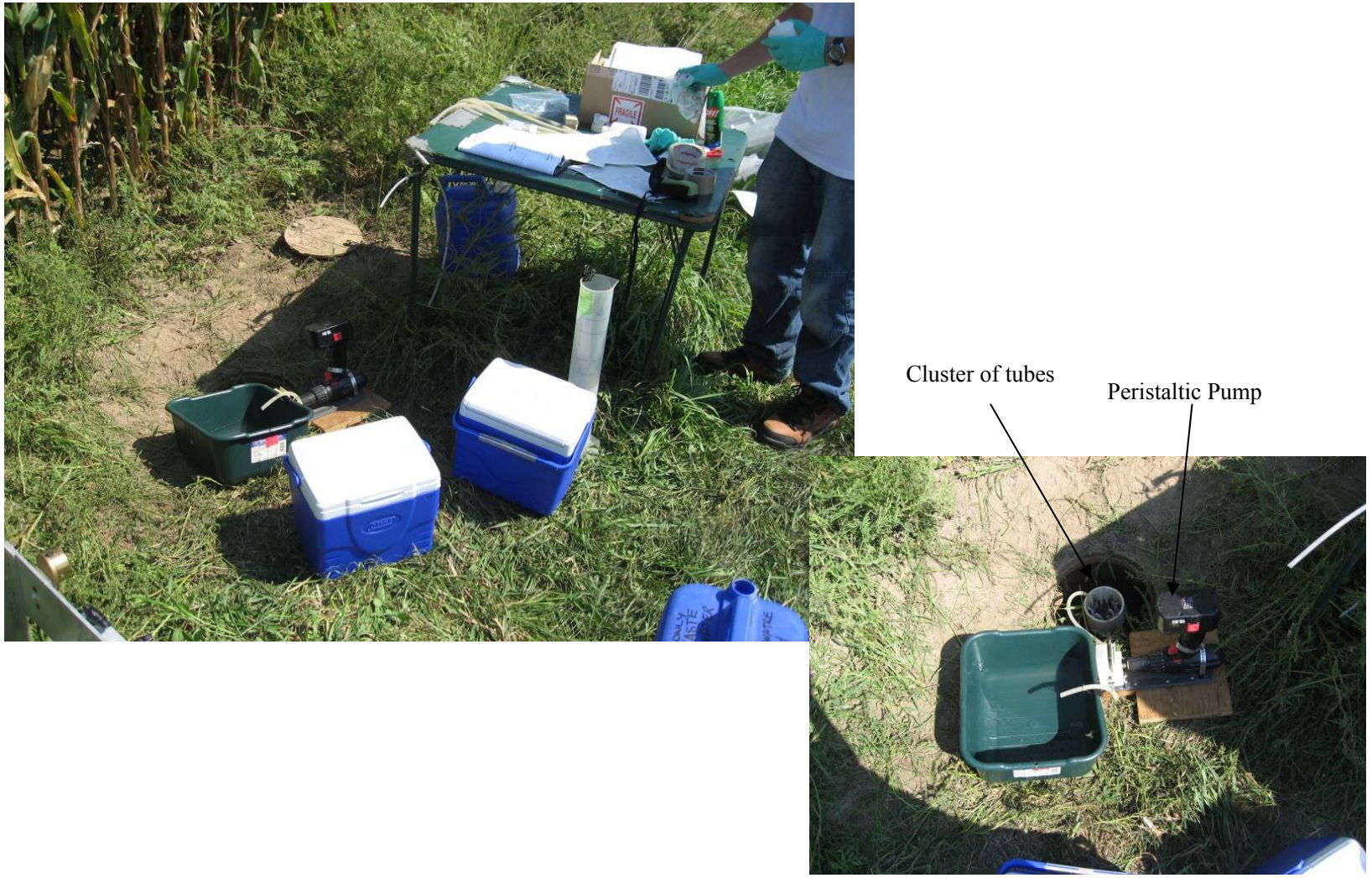


Figure 4.8 Sampling in Waterloo Multilevel Well MP-8
MP-8 was a Waterloo Multilevel system installed by University of Waterloo. Each sampling port had a dedicated tube to the ground surface. Sampling was done by pumping groundwater using a peristaltic pump.

Table 4-1 Selected Sampling Locations for the Sampling Round in September 2007

	GeoTrans Wells	UW Multilevel Wells Ports
Sampling Locations	MW-49R,P-53,P-94,MP-3-1,P-157, P-151,MP-3-2,P-95,P-108,P-152, MP-3-4,P-90,P-115,P-71,P-70,P-164, P-129,P-145,P-156,P-116,P-131,P-153, P-132,P-160,P-136,P-140,P-138	MP-6-37,MP-6-31,MP-6-30,MP-6-29, MP-6-27,MP-6-23,MP-6-17, MP-8-12,MP-8-11,MP-8-10,MP-8-9,MP-8-7, MP-8-5,MP-8-3

Note that GeoTrans wells include mainly conventional wells as well as one multilevel well MP-3. MW-49R does not have a dedicated pump inside while other conventional wells do.

Table 4-2 Layer Number of the Sampling Locations

Well ID	Layer Number	Well ID	Layer Number	Well ID	Layer Number
MW-49R	1	MP-6-30	4-5	P-160	5
P-53	2	MP-3-4	5	P-136	5
P-94	2	P-90	5	P-140	5
MP-3-1	3	P-115	5	P-138	5
P-157	3	P-71	5	MP-6-29	5
P-151	3	P-70	5	MP-6-27	5
MP-6-37	3	P-164	5	MP-8-10	5
MP-8-12	3	P-129	5	MP-8-9	5
MP-3-2	4	P-145	5	MP-6-23	6
P-95	4	P-156	5	MP-6-17	6
P-108	4	P-116	5	MP-8-7	6
P-152	4	P-131	5	MP-8-5	6
MP-6-31	4	P-153	5	MP-8-3	6
MP-8-11	4	P-132	5		

Note that MP-6-30 is at the interface of Layer 4 and Layer 5, therefore the layer number is referred to as 4-5.

Table 4-3 Sampling and Storing Methods for Each Analysis

Parameter	Container	Preservative	Headspace	Filter (0.45 μm)	Storing Method
^{13}C (chlorinated ethenes)	Four 40ml glass vials	4 drops of NaOH*	NO	NO	Cooler (ice pakcs)
^{37}Cl (chlorinated ethenes)	Four 40ml glass vials	4 drops of NaOH	NO	NO	Cooler(ice packs)
VOCs and Dissolved Gases (methane, ethene and ethane)	One 40ml glass vial	NaOH	NO	NO	Cooler (ice packs)
Cations	250ml polyethylene bottle	2ml Nitric Acid*	yes	yes	Cooler (ice packs)
Anions	250ml polyethylene bottle	no	yes	no	Cooler (ice packs)

*The concentration of NaOH solution is 10N.

** The concentration of Nitric acid is 35 percent.

4.2 Analytical Methods

Groundwater samples were sent to different laboratories for analyses including VOCs, dissolved gases, cations, anions, and carbon isotopes. Three 40ml vials were collected by the consultant for VOCs analysis. One 40ml vial was collected by the University of Waterloo personnel for analysis of major chlorinated compounds and dissolved gases. Four 40ml vials were collected for carbon isotopes analysis and two 250ml polyethylene bottles were collected for cations and anions analyses.

4.2.1 Inorganics

Analyses of the following inorganics were performed: Cl, SO_4, HCO_3, Fe, Mn, Ca, Mg, Na, K, and Si. The analyses were done at the environmental laboratory of SGS Canada Inc.

Three different analytical methods, Ion chromatography, Titration, and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), were used for the analyses of these inorganics. These methods were briefly described as follows:

Ion chromatography is a form of liquid chromatography. It measures concentrations of ionic species by separating them based on their interaction with a resin. Ionic species separate differently depending on species type and size. Sample solutions pass through a pressurized chromatographic column where ions are absorbed by column constituents. As an ion extraction liquid, known as eluent, runs through the column, the absorbed ions begin separating from the column. The retention time of different species determines the ionic concentrations in the sample.

Titration is a laboratory technique by which the concentration of an unknown reagent is determined using a standard concentration of another reagent that chemically reacts with the unknown.

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is an analytical technique used for the detection of trace metals. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample.

The analytical methods and Method Detection Limits for each method provided by SGS Canada Inc. are listed in Table 4-4.

4.2.2 VOCs

The groundwater samples collected by the consulting company were sent to Pace Analytical Services, Inc. for analysis of 35 compounds. The protocol for VOCs analysis refers to the EPA Method 8260B, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS).

The groundwater samples collected by the UW personnel were sent the Institute for Groundwater Research at University of Waterloo (Gillham lab). Analysis focused on chlorinated ethenes including PCE, TCE, cis-DCE, trans-DCE , 1,1-DCE, and VC. The method detection limits (MDL) were given in Table 4-5.

For PCE and TCE analysis, the following protocol was used. A 2.0mL sample was removed and added to 2 ml of internal standard solution (500 μg/L of 1,2-Dibromoethane in pentane) in a 5ml glass screw cap vial with Teflon-faced septum. The sample was placed on an orbital shaker for 15 minutes at 300 RPM. The supernatant was then removed, placed in a 2 mL glass crimp-top GC vial and put on a Hewlett Packard 5890 Series II gas chromatograph equipped with a Ni63 ECD detector. Using a HP 7673 liquid auto sampler a 1uL sample was injected onto a DB-624 capillary column. The detector temperature was 300℃, injection temperature was 200℃ and the column temperature ramped up from 50℃ to 150℃ at a rate of 15℃/min and then held for 1 min. The carrier gas was pre-purified helium with a total flow rate of 25 mL/min and the make-up gas was 5 percent methane, 95 percent argon.

For VC, cis-DCE, 11DCE and trans-DCE analysis the following protocol was used. A headspace was created in the aqueous samples with a ratio of 6.0 mL headspace to 4.0 mL aqueous sample. The samples were placed on a rotary shaker for 15 minutes to allow equilibration between the water phase and gas phase. For analysis, the sample was placed on a Hewlett Packard 7694 headspace Sampler. A 1mL sample was then injected

onto a Hewlett Packard 5890 gas chromatograph (GC) equipped with an Hnu Photo ionization detector (PID) using an Hnu NSW-plot capillary column. The lamp potential was 10.2 eV. The GC had an initial temperature of 50℃, with a temperature program of 20℃/min reaching a final temperature of 200℃ and was then held at 200℃ for 9 minutes. The detector and injector temperatures were 150℃ and 100℃, respectively. The carrier gas was ultra pure Helium with a flow rate of 20 mL/min.

4.2.3 Dissolved Gases

Dissolved Gases analysis was also done at the Institute for Groundwater Research at the University of Waterloo (Gillham lab). Methane, ethene, ethyne and ethane were analyzed. The method detection limits (MDL) were given in Table 4-5.

The following protocol was used for the analysis. A headspace was created in the aqueous samples with a ratio of 2.5 mL headspace to 2.5 mL aqueous sample. The samples were placed on a rotary shaker for 15 minutes to allow equilibration between the water phase and gas phase. For analysis, a 250uL sample was then injected onto a Hewlett Packard 5790 gas chromatograph (GC) equipped with an flame ionization detector (FID) using a GS-Q plot capillary column. The GC had an initial temperature of 60℃, which was held for 3 minutes; the temperature was then increased at a rate of 15℃ /min to a final temperature of 120℃ and then was held at 125℃ for 10 minutes. The detector and injector temperatures were set for 280℃ and 120℃, respectively. The carrier gas was ultra pure nitrogen with a flow rate of 20 mL/min.

4.2.4 Carbon Isotopes

Carbon isotope analysis was performed by Ziheng Miao at the Environmental Isotope Laboratory at the University of Waterloo. Samples were analyzed using a Gas Chromatograph Combustion Isotope Ratio Mass Spectrometer (GC-C-IRMS). The GC-C-IRMS system consisted of an Agilent 6890 GC (Agilent, Palo Alto, U.S.A.) with a split/splitless injector, a Micromass combustion interface operated at 850 ℃, a cold trap cooled to -100℃ using liquid nitrogen, and a Micromas Isoprime isotope-ratio mass spectrometer (Micromass, Manchester, U.K.). Solid Phase Microetraction (SPME) technique was used to extract and inject the contaminants. The SPME uses a fiber assembly and a holder equipped with a 75μm Carboxen PDMA black fiber, which can effectively adsorb VOC at room temperature and desorb VOC at high temperature.

First, samples were prepared for extraction by diluting certain amount of groundwater sample to a concentration close to 100 ppb in another clean 40ml vial to about 35ml, leaving a moderate headspace for inserting the SPME fiber. The approximate amount of sample needed for dilution was calculated by the following equation:

$$\text{Sample Volume}=35\text{ml}\times\frac{100\text{ppb}}{C_0}$$

where C_0 was the concentration of the sample. For samples with a concentration of the target compound lower than 100 ppb, no dilution was performed; instead, salt was added to the extraction vial to expel the contaminants from the water into the air. To prepare the extraction vial, a clean vial with a magnetic stir bar inside was added the calculated amount of sample with a syringe and filled to 35 ml with nano-pure water. A Teflon/silicon septum and a plastic cap were then quickly placed on the vial. The vial was put on a stir plate to form a whirlpool at the top. A SPME fiber (baked before use) was penetrated through the septum into the whirlpool and was left for extraction for 20

minutes. Then it was inserted into the GC for desorption for 3 min after the analysis started.

The GC analysis was done at a split ratio of 1:3, with a column flow rate of 1ml/min in the Constant Flow mode. A RTX-5 column was used (30 m length, 0.25mm internal diameter, 1m stationary phase, from Restex Corporation, Bellefonte, PA, U.S.A.).

For the samples containing only PCE and TCE, the following oven temperature program was used: 50℃ for 2 min, 20℃/min to 200℃, hold time at 200℃ for 5 min, and the injector was set at 310℃. For the other samples the following oven temperature program was used: 50℃ for 2 min, 12℃/min to 200℃, hold time at 200℃ for 5 min, and the injector was set at 310℃.

Carbon isotopes analysis of PCE, TCE, cis-DCE, 1,1-DCE, 1,1,1-TCA, and 1,1-DCA were performed. PCE and TCE were analyzed only in a couple of samples due to low concentrations while cis-DCE, 1,1-DCE, 1,1,1-TCA, 1,1-DCA were analyzed in many of the samples. All $^{13}C/^{12}C$ ratios are reported in the delta notation ($\delta^{13}C$) referenced to the VPDB (Vienna Peedee Belemnite) standard.

Table 4-4 Techniques and Method Detection Limit for the Analyses of Inorganic Species

Parameter	Technique	MDL** (mg/l)
Cl	Ion Chromatography	0.2
SO4	Ion Chromatography	0.5
HCO3	Titration	1
Fe	ICP-OES*	0.01
Mn	ICP-OES	0.001
Ca	ICP-OES	0.03
Mg	ICP-OES	0.003
Na	ICP-OES	0.01
K	ICP-OES	0.01
Si	ICP-OES	0.01

(From SGS Canada Inc.)

*ICP-OES is short for Inductively Coupled Plasma - Optical Emission Spectrometer

** MDL is short for Method Detection Limit

Table 4-5 Method Detection Limit for the Analyses of VOCs and Dissolved Gases (UW)

			TCE	PCE		VC	11DCE	tDCE	cDCE		methane	ethene	Ethyne	ethane
	MDL(ug/L)		0.6	0.9		1.3	3.9	2.3	1.9		0.5	0.5	3.1	0.4

5 Results

5.1 Historical Data Review

5.1.1 Contaminant Concentrations in Well MP-3-4

From 1992 to the present, with the exception of 1993 to 1995, when no sampling occurred, quarterly sampling (usually in March, June, September, and December) was carried out. In each sampling round, groundwater was sampled and analyzed for more than 30 compounds. The network of monitoring wells has been increasing as the plume has extended and its position is better understood. Most of the monitoring activities have focused in Layer 5.

The long term VOCs concentration pattern in the area downgradient to the source was first evaluated using the data collected from 1992 to April 2007 in the well MP-3-4. Well MP-3-4 was selected because it represented most of the contaminant mass in Layer 5 and its position was on the main flow direction very near the DNAPL source (Figure 4.3).

The total concentration of chlorinated ethenes within MP-3-4 was around 50,000 μg/L in 1992 (Figure 5.1). Data was not collected from 1993 to 1995. From 1996 to June 1998 the total concentration was around 10,000 μg/L. Before June 1998, little cis-DCE (degradation product from TCE) can be observed. In September 1998, the total concentration increased drastically to more than 80,000 μg/L, which was eight times of the concentration in June 1998 (Figure 5.1). The total concentration peaked in December 1998 with a value of 162,470 μg/L and declined to about 80,000 μg/L in March and June 1999. During September 1998 to June 1999, the composition of chlorinated ethenes was still mainly TCE and PCE with little degradation to cis-DCE (Figure 5.1). The total concentration of chlorinated ethenes increased again to 149,700 μg/L in September 1999

and continued to be such high until December 2005. After this date the concentration decreased to about 100,000μg/L in 2006 and 2007. Degradation of PCE/TCE to cis-DCE started around September 1999 and was completed at the end of 2002 (Figure 5.1).

The total concentration of chlorinated ethanes within well MP-3-4 was about 60,000 μ g/L in 1992 (Figure 5.2). Data was not collected between 1993 and 1995. The total concentration was relatively low between 1996 and June 1998, with values around 10,000 μ g/L, increased sharply to 130,000 μ g/L in September 1998 and peaked in December 1998 with a value of 220,230 μ g/L (Figure 5.2), which is very consistent with the concentration increase of chlorinated ethenes (Figure 5.1). The total concentration declined in March 1999 to about 100,000 μ g/L and maintained the same level until the end of 2004. After this time, the concentration was around 50,000 μ g/L (Figure 5.2). The production of 1,1-DCA from degradation of 1,1,1-TCA started in September 1999, which was exactly the same time as the start of the production of cis-DCE from TCE. But almost complete degradation from 1,1,1-TCA to 1,1-DCA (about 95%) was not achieved until about 2004 (Figure 5.2), which was about two years later than the almost complete degradation of PCE/TCE to cis-DCE.

The occurrence of the major increases of chlorinated compound concentration is thought to be induced by the DNAPL pumping in the source zone in Layer 5. Large-scale DNAPL pumping was performed during 1999 to 2002, as mentioned in section 3.1, but actually before that period DNAPL pumping was performed in the recovery well RW-58 (position shown in Figure 5.3) during the months of August through October 1998 (HSI GeoTrans, 1999) (referred to as a pilot DNAPL pumping in this thesis). The pilot DNAPL pumping in well RW-58 corresponded very well with the subsequent concentration peaking in the well MP-3-4, just downgradient to the source zone observed in September and December 1998 (Figure 5.1 and Figure 5.2). After the pilot DNAPL

pumping in well RW-58, the next DNAPL pumping (which was the start of large scale DNAPL pumping) was performed in seven recovery wells (RW-110 through RW-114, OW-57 and RW-58, positions shown in Figure 5.3) conducted during the months of August through the first week of November 1999 (HSI GeoTrans, 1999). The large scale DNAPL pumping corresponded very well with the chlorinated ethenes concentration peaking in well MP-3-4 in September 1999 (Figure 5.1). It is thought that the DNAPL pumping in the source zone in Layer 5 reduced the volume of the DNAPL pool and opened at least some of the groundwater flow channels, resulting in groundwater flowing much more freely through the source zone to the downgradient areas (where well MP-3-4 was located). The increased contact area between the DNAPL and the groundwater caused the huge increases in contaminant concentration after DNAPL pumping. It was noted that the concentration change of chlorinated ethanes was not very similar to that of chlorinated ethenes, reflecting a mixing of DNAPLs that had different compositions from different parts of the DNAPL source zone by the DNAPL pumping.

The DNAPL pumping also caused huge increases in the concentrations of BTEX and especially of the ketones in the well MP-3-4 (Figure 5.4). After the pilot DNAPL pumping in the recovery well RW-58 was performed during the months of August through October 1998, a small peak of BTEX concentration appeared in December 1998 and a small peak of ketones concentration appeared a little later in March 1999. The large scale DNAPL pumping during the months of August through the first week of November 1999 caused a more significant increase of the concentrations of BTEX and especially of the ketones. The BTEX concentration increased to 81,000 µ g/L in December 1999 and remained to be high thereafter (Figure 5.4). The ketones concentration increased dramatically to 640,000 µ g/L in September 1999 and peaked in March 2000 with a value of 890,000 µ g/L. After that, the ketones concentration declined to 283,000 µ g/L in July

2002 and remained at the same level until July 2005. After this period it declined to less than 100,000 μ g/L, which was still high comparing with the concentrations of total chlorinated compounds and BTEX (Figure 5.4). It is proposed that the huge amounts of ketones and BTEX were probably pumped into Layer 5 from the upper layers since ketones and BTEX are less dense than water.

Most importantly, it was noted that the significant increase of degradation of TCE to cis-DCE and 1,1,1-TCA to 1,1-DCA starting from September 1999 (Figure 5.1 and Figure 5.2) exactly corresponded to the time of huge increase of ketones concentration (Figure 5.4). This is strong evidence that the ketones and BTEX caused the significant degradation of TCE to cis-DCE and 1,1,1-TCA to cis-DCE by serving as electron donors, which made the aquifer enough reducing for biodegradation of TCE to cis-DCE, and also provide the substrates for the microorganisms. It was also noted that the small peaks of concentrations of BTEX and ketones after the pilot DNAPL pumping in RW-58 in 1998 did not induce an increase of degradation of TCE to cis-DCE or 1,1,1-TCA to 1,1-DCA, indicating that the BTEX and ketones concentrations were not enough to created the optimal condition for biodegradation of chlorinated compounds in the aquifer.

The decrease of concentrations that were observed for all the compounds, chlorinated ethenes and ethanes, ketones, and BTEX, was probably caused by the groundwater pumping in the Hydraulic Barrier System which includes four extraction wells in the middle of the plume in Layer 5 which has been in operation since October 2003.

Summarizing, based on the data collected in Layer 5, specifically in well MP-3-4 located near the source, the long term behavior of the contaminants after 1992 can be generally divided into three stages: before DNAPL pumping (1992 to June 1998), after DNAPL pumping in RW-58 during the months of August through October 1998

(September 1998 to June 1999), and after large scale DNAPL pumping during the months of August through the first week of November 1999 (September 1999 to the present). The first stage was characterized by relatively low total concentrations of chlorinated ethenes and ethanes with almost no degradation to cis-DCE and 1,1-DCA and almost no BTEX and ketones. The second stage was characterized by relatively high total concentrations of chlorinated ethenes and ethanes with almost no degradation to cis-DCE and 1,1-DCA and small amounts of BTEX and ketones. The third stage was characterized by relatively high total concentrations of VOC with a significant degradation of PCE/TCE to cis-DCE and 1,1,1-TCA to 1,1-DCA.

5.1.2 Plume History

Data collected during selected sampling events were used to evaluate the long term pattern of the spatial distribution of the contaminant mass and the degradation history in Layer 5. These events correspond to the following sampling rounds: June 1998 (just before DNAPL pumping), June 1999 (after the first pilot DNAPL pumping in well RW-58 and just before the large scale DNAPL pumping), June 2001 (during the large scale DNAPL pumping from 1999 to 2002 and significant degradation to cis-DCE and 1,1-DCA in Layer 5 had occurred), and June 2006 (recent year showing that PCE/TCE were almost completely degraded to cis-DCE and 1,1,1-TCA was also significantly degraded to 1,1-DCA).

Chlorinated Ethenes in Layer 5 In June 1998, before the DNAPL pumping started, the spatial distribution of chlorinated ethenes includes three areas that had distinct concentrations and degradation extents (Figure 5.5). The area near the source, where MP-3-4 was located, had the highest VOCs concentrations (12,100 µg/L in June 1998) compared to the other wells, almost no BTEX or ketones, and minor degradation to cis-DCE (less than 5%) (Figure 5.5). The area to the south and southeast of the source zone had low VOCs concentrations (all less than 880 µg/L in June 1998) and a greater extent of degradation primarily to cis-DCE (Figure 5.5). The area further to the east, where wells P-71 and P-70 were located, had very low concentrations (9 µg/L and 0 µg/L, respectively, in June 1998) of primarily TCE with minor degradation to cis-DCE (Figure 5.5). The very low concentration in this area indicated the presence of a short plume of chlorinated ethene in the eastward direction, which was supposed to be the main flow direction. It is likely that the very limited plume length in the eastward direction was caused by groundwater bypassing the bulk of the DNAPL (Austin, 2005), because of the low permeability of the water in this DNAPL saturated zone before

DNAPL pumping in the source zone. The concentrations of chlorinated ethenes fluctuated significantly in most of the wells during April 1992 (or the time of well installation) to June 1998 (Figure 5.5). However, the dominant component/components in each well did not change much and the relative concentrations between the wells remained constant, indicating that the pattern of chlorinated ethenes concentration and composition distribution was relatively stable before June 1998.

In June 1999 (Figure 5.6), which was after the first pilot DNAPL pumping in well RW-58 during August through October in 1998 and just before the large scale DNAPL pumping, the concentration of total chlorinated ethenes in the area near the source in well MP-3-4 (84,200 μ g/L) was almost eight times of the concentration in June 1998, which was just before the pilot DNAPL pumping. This was already observed in the time plot for well MP-3-4 (Figure 5.1). Undetectable cis-DCE and 1,1-DCA concentrations were found in this area, which were even lower than the concentrations before June 1998. A small amount of ketones (1,000 μ g/L) and a moderate amount of BTEX (24,000 μ g/L) were found in this area. As mentioned before, this huge increase of total concentration of chlorinated ethenes was caused by the pilot DNAPL pumping in recovery well RW-58 during the months of August through October and the DNAPL pumping also drew a small amount of ketones and a moderate amount of BTEX into Layer 5. The influence of the DNAPL pumping was also detected in the area further to the east in well P-71, which had an increase of total chlorinated ethenes concentration from 9 μ g/L to 291 μ g/L (Figure 5.6). But well P-70 just nearby, still had a zero concentration and was not affected by the DNAPL pumping. The composition of chlorinated ethenes in P-71 was almost entirely TCE and PCE as compared to about 15% cis-DCE in June 1998. This decrease of the extent of degradation to cis-DCE in the area further to the east and also in the area near the source (in well MP-3-4) was probably caused by flushing of newly

dissolved TCE and PCE from the source to the east after the DNAPL pumping. Although the total concentration of chlorinated ethenes in the areas near the source and further to the east increased significantly after the pilot DNAPL pumping in 1998, the plume of chlorinated ethenes in the eastward direction seemed to be still very limited, inferred from the relatively low concentrations in wells P-71 and especially in P-70, compared to well MP-3-4 (Figure 5.6). The southern part of the plume (to the south of the source zone) had relatively low concentrations of primarily cis-DCE (Figure 5.6), which was very similar to June 1998 (Figure 5.5).

After the large-scale DNAPL pumping during the months of August through the first week of November in 1999, a major increase of contaminant concentrations and degradation products was observed extending far away to the east in June 2001 (Figure 5.7), compared to June 1999. The area near the source had a concentration of 170,400 μg/L in well MP-3-4, compared to 84,200 μg/L in June 1999. The area further to the east had concentrations of 71,740 μg/L, 109,730 μg/L, and 35,820 μg/L, in the wells P-71, P-115, and P-70 respectively (Figure 5.7), compared to 291 μg/L in P-71 and 0 in P-70 in June 1999. The chlorinated ethenes in the area near the source in well MP-3-4 had evolved to almost 40% being composed of cis-DCE and half of TCE, compared to entirely TCE and PCE in June 1999. The composition of chlorinated ethenes in the area further to the east in well P-71 became almost entirely cis-DCE, compared to entirely PCE and TCE in 1999. Even further than the well P-71, in the middle of the plume, concentrations were thousands of μg/L and compositions were mainly cis-DCE (Figure 5.7). In addition to the chlorinated ethenes, large amounts of ketones (425,000 μg/L) and BTEX (76,500 μg/L) emerged in the area near the source in well MP-3-4, which was

likely the reason for the start of large-scale degradation of chlorinated ethenes in Layer 5 as stated before.

Long time after the large-scale DNAPL pumping, in 2006, the concentrations in these areas decreased significantly to 53,080 µ g/L, 39,530 µ g/L, 5,750 µ g/L, and 30 µ g/L in wells MP-3-4, P-115, P-71, and P-70, respectively (Figure 5.8). The decrease was probably due to groundwater extraction in the middle of the plume by the Hydraulic Barrier System which started to operate in October 2003. Concentrations of ketones and BTEX also decreased but the proportions were still high in the area near the source. The composition of chlorinated ethenes in the areas near the source and further to the east continued to have increasing cis-DCE (Figure 5.8). The percentage of cis-DCE in MP-3-4 evolved from 40% in 2001 (Figure 5.7) to more than 98% in 2006 (Figure 5.8). The wells located in the middle of the plume start to have further degradation products such as VC and ethene and the wells located at the edge of the plume started to have cis-DCE in June 2006.

It was noted that the composition of chlorinated ethenes at the edge of the plume was primarily composed of TCE and PCE in the years after 2001, as compared to the composition in the middle of the plume which was primarily composed of cis-DCE. This pattern of composition and distribution of chlorinated ethenes was contrary to the expected pattern of increasing proportion of degradation products along the flow path, as stated in section 1.2 for degradation of chlorinated ethenes (Figure 1.2). It was noted that the composition in the northern part of the plume in 2001, which was primarily TCE and PCE (Figure 5.7), seemed to be linked with the composition in the upgradient wells MP-3-4 and P-71 in 1999 (Figure 5.6). This observation suggested that this pattern of VOC composition and distribution was probably caused by the transport of PCE and

TCE from the upgradient area to the edge of the plume before significant degradation started in the areas near the source.

Chlorinated Ethanes in Layer 5 The distribution of chlorinated ethanes in Layer 5 had a very similar pattern as chlorinated ethenes. The area near the source to the east always had the highest concentrations of chlorinated ethanes compared to the area south of the source, which had low concentrations. Before DNAPL pumping, the plume of chlorinated ethanes to the east was very limited, inferred from very low concentrations in P-71 and P-70, 6 and 0 μg/L observed in June 1998, respectively (Figure 5.9). After the first pilot DNAPL pumping in August through October in 1998, the concentration of chlorinated ethanes in the area near the source zone in well MP-3-4 increased dramatically to 120,000 μg/L in June 1999 (Figure 5.10), compared to 9,710 μg/L in June 1998. However, the plume was still short to the east, indicated from relatively low concentrations in P-71 and P-70 (271 and 0 μg/L, respectively) (Figure 5.10). After the large-scale DNAPL pumping during the months of August through the first week of November in 1999, the concentrations of chlorinated ethanes in the area to the east of the source increased significantly and the plume extended far to the east in June 2001 (Figure 5.11). The concentrations declined in June 2006 probably due to the groundwater pumping in the Hydraulic Barrier System operated since October 2003 (Figure 5.12). The concentrations of chlorinated ethanes were always at the same order of magnitude as the concentration of chlorinated ethenes. However, degradation of chlorinated ethanes after the large-scale DNAPL pumping in 1999, which introduced large amounts of BTEX and ketones into Layer 5, was delayed relative to degradation of chlorinated ethenes. In June 1998 and June 1999 before the large scale DNAPL pumping, appreciable degradation (about 60%) was only found in the area to the south of the source zone in well MP-2-4, which was consistent with the great degradation degree of chlorinated ethenes to

cis-DCE in the same area at the same time. In June 2001, almost two years after the large-scale DNAPL pumping, the greatest degree of degradation in the high concentration zone to the east of the source was found to be only about 30% in well P-71. In June 2006, almost complete degradation of 1,1,1-TCA to 1,1-DCA was found in the area near the source zone in MP-3-4 and P-115 and in the middle of the plume the degree of degradation was generally less than 50% (Figure 5.12). Degradation of 1,1-DCA to chloroethane was observed in few wells. Thus, the degradation of 1,1,1-TCA occurred more slow and more gradually than the degradation of TCE within Layer 5, indicating that 1,1,1-TCA is more recalcitrant than TCE.

Contaminants in Layer 2 The VOC Plume in Layer 2 was confined to the area near the source zone and it seems to be controlled by the presence of a pond where the plume discharge and concentration are affected by natural processes such as dilution and volatilization (Swanson et al., 2005). VOC concentrations in Layer 2 were generally very high, with the highest concentrations being 244,400 μ g/L and four wells having concentrations around 100,000 μ g/L in 1992. The concentrations decreased over time from 1992 to 2006, though the trend is not very clear due to variability in sampling locations. The decrease of the concentrations might be related to degradation and the soil vapor extraction (SVE) in the vadose zone that was performed in 1998. The composition of chlorinated ethenes changed gradually from primarily TCE and cis-DCE in the early years to primarily cis-DCE and VC in the recent years. During all the sampling years, there were always high concentrations of BTEX and ketones in Layer 2 (Figure 5.13, June 1999 before large-scale DNAPL pumping in Layer 5), corresponding to much greater degree of degradation than Layer 5. The presence of high concentrations of BTEX and ketones in Layer 2 in the early years (before the DNAPL pumping in Layer 5)

indicated accumulation of these lighter organic contaminants in the upper layers before the DNAPL pumping.

The pattern of concentration change of chlorinated ethanes in Layer 2 was similar to that of chlorinated ethenes. The concentrations were relatively higher in the early years and decreased over time. From 1992 to 1996 degradation of 1,1,1-TCA to 1,1-DCA was incomplete in almost all the wells. In 2001, complete degradation of 1,1,1-TCA to 1,1-DCA was observed in many of the wells and significant amounts of chloroethane were found in two of the wells. There were only a few wells sampled in 2006. However, degradation of 1,1,1-TCA to 1,1-DCA was completed and significant amount of chloroethane was observed in all the wells.

The degradation of chlorinated ethenes seemed to occur at a faster rate than that of chlorinated ethanes within Layer 2, as was the case in Layer 5. Degradation of chlorinated ethanes in Layer 2 showed a greater degree than in Layer 5 in all the sampling years, similarly to the degradation of chlorinated ethenes, again caused by earlier presence of BTEX and ketones in Layer 2 than in Layer 5.

Origin of 1,1-DCE The concentration of 1,1-DCE was relatively low, ranging from 0 to about 5,000 μg/L within the well MP-3-4 (Figure 5.1). The percentage of 1,1-DCE out of the total chlorinated compounds in MP-3-4 has been around 1.7 percent (average) throughout most of the sampling years even after significant degradation of chlorinated ethenes or ethanes occurred (Figure 5.14), indicating no significant production of 1,1-DCE from degradation of TCE or 1,1,1-TCA. It was shown in section 3.4 that 1,1-DCE in the DNAPL was about 0.16 percent. Using Raoult's law and the solubility for each compound in the DNAPL, the percentage of 1,1-DCE out of the total chlorinated compounds from dissolution of the DNAPL was calculated to be 2.2 percent which is very close to the average percentage of 1,1-DCE found within MP-3-4. This strongly

suggested that 1,1-DCE was from the dissolution of the DNAPL, not from biodegradation of TCE or abiotic degradation of 1,1,1-TCA, as stated in Section 1.2 for degradation pathways (Figure 1.1).

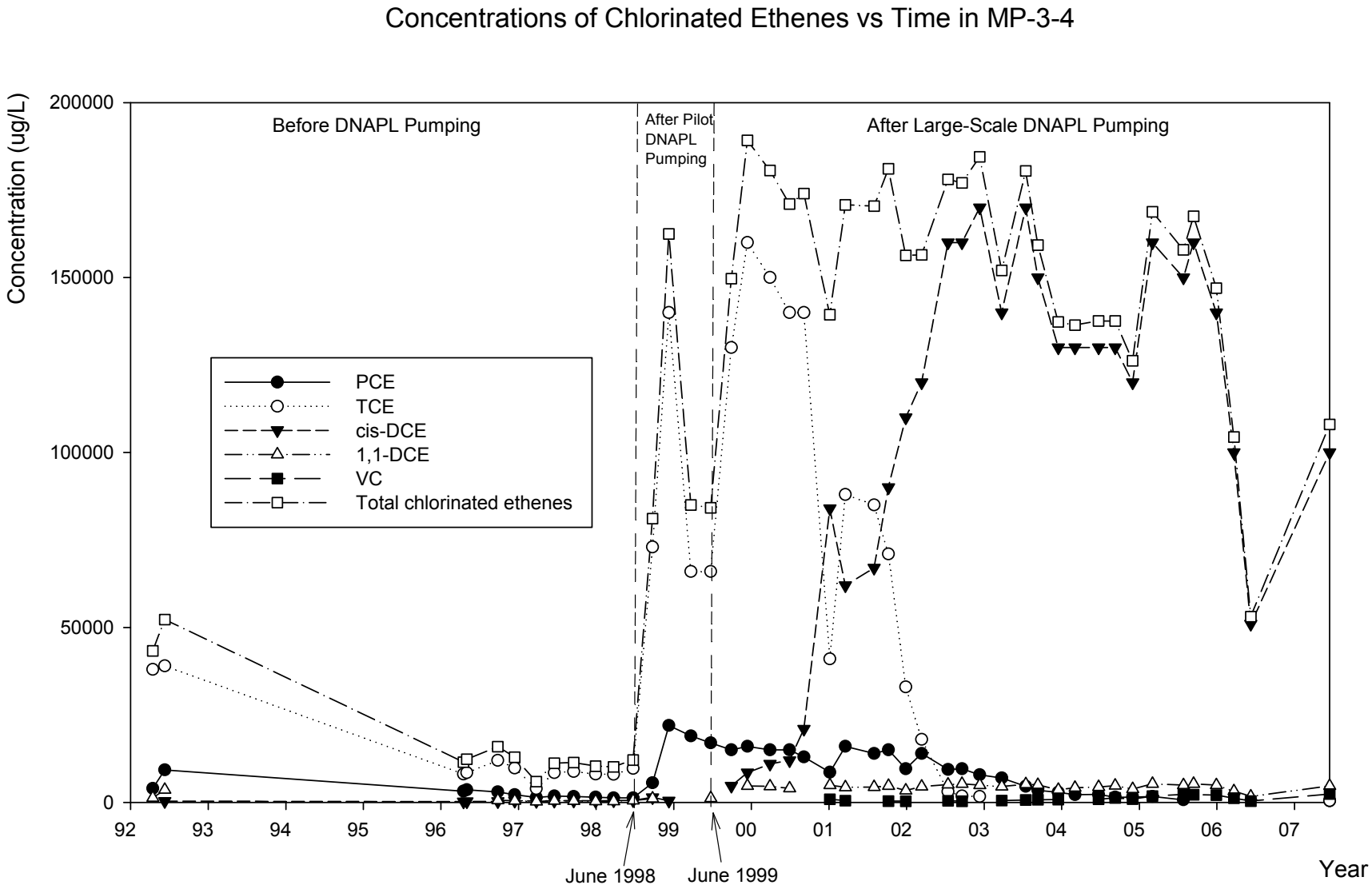


Figure 5.1 Concentration and Composition of Chlorinated Ethenes in MP-3-4 from 1992 to June 2007
Well MP-3-4 is located near the source on the main groundwater flow direction.

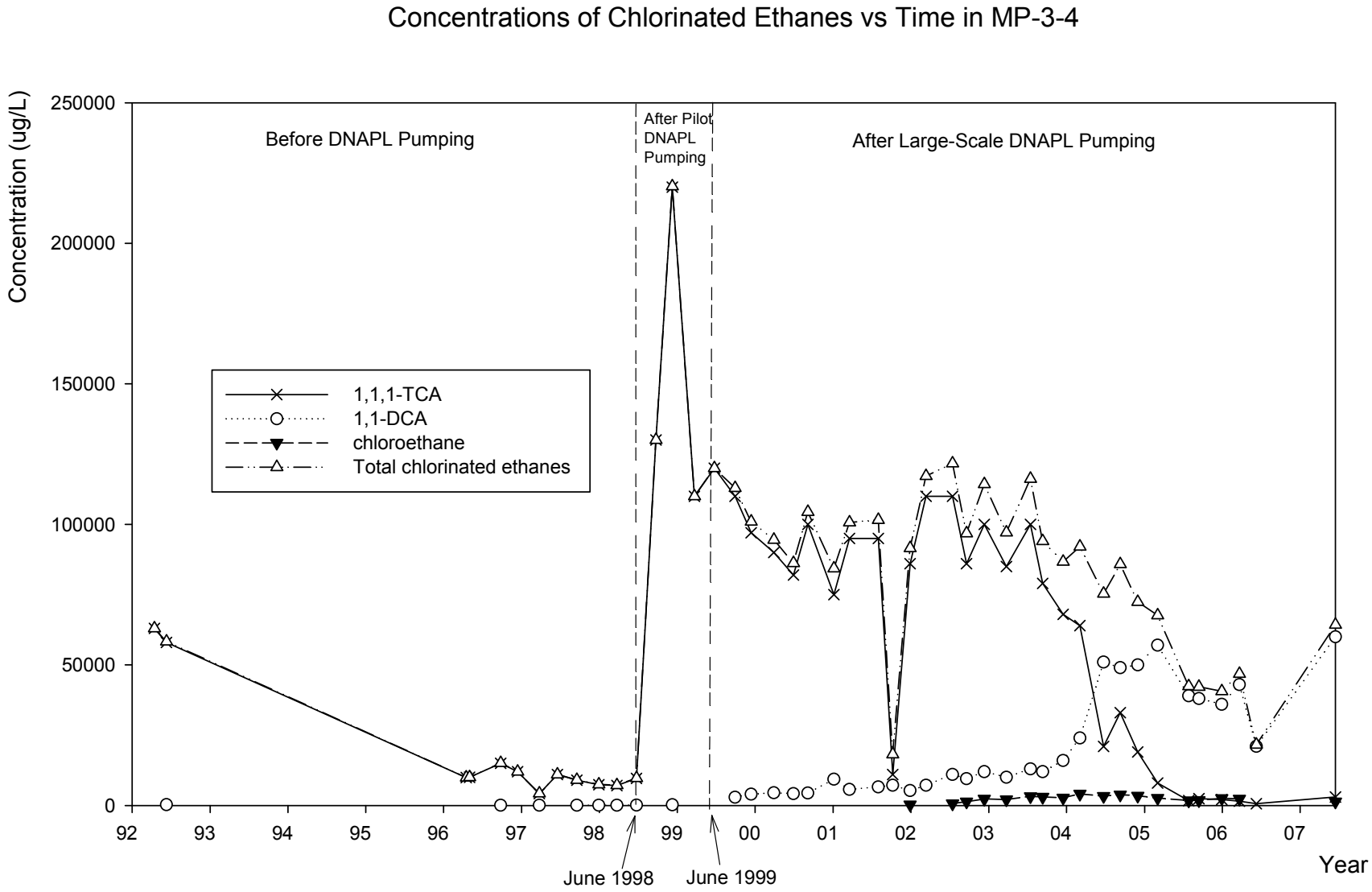


Figure 5.2 Concentrations of Chlorinated Ethanes in MP-3-4 from 1992 to 2007
Well MP-3-4 is located near the source on the main groundwater flow direction.

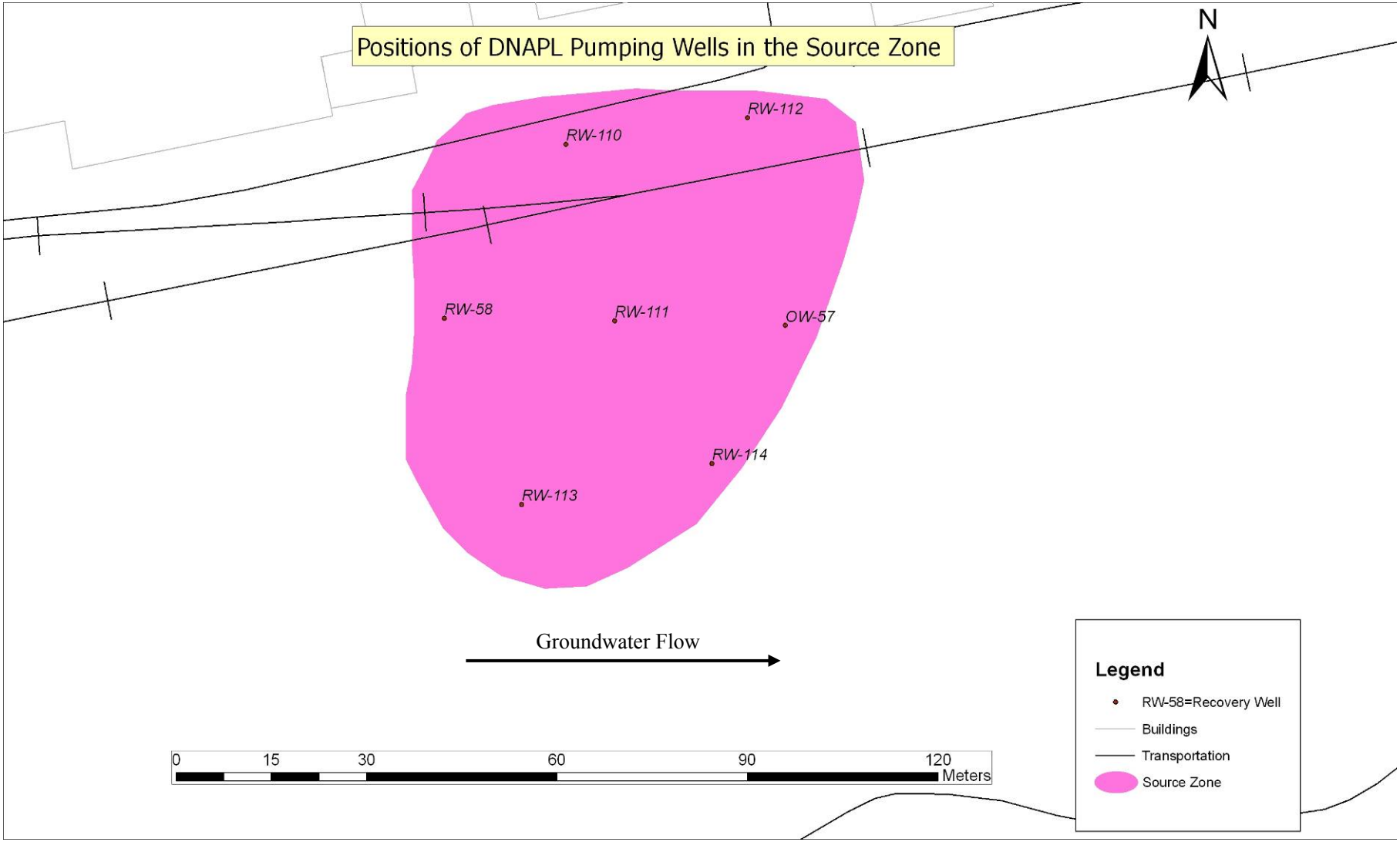


Figure 5.3 Positions of DNAPL Pumping Wells in the Source Zone

DNAPL pumping was first performed in the recovery well RW-58 during the months of August through October 1998 (HSI GeoTrans, 1999) (referred to as pilot DNAPL pumping in this thesis). The next DNAPL pumping (large scale) was performed in seven recovery wells (RW-110 through RW-114, OW-57 and RW-58) during the months of August through the first week of November 1999

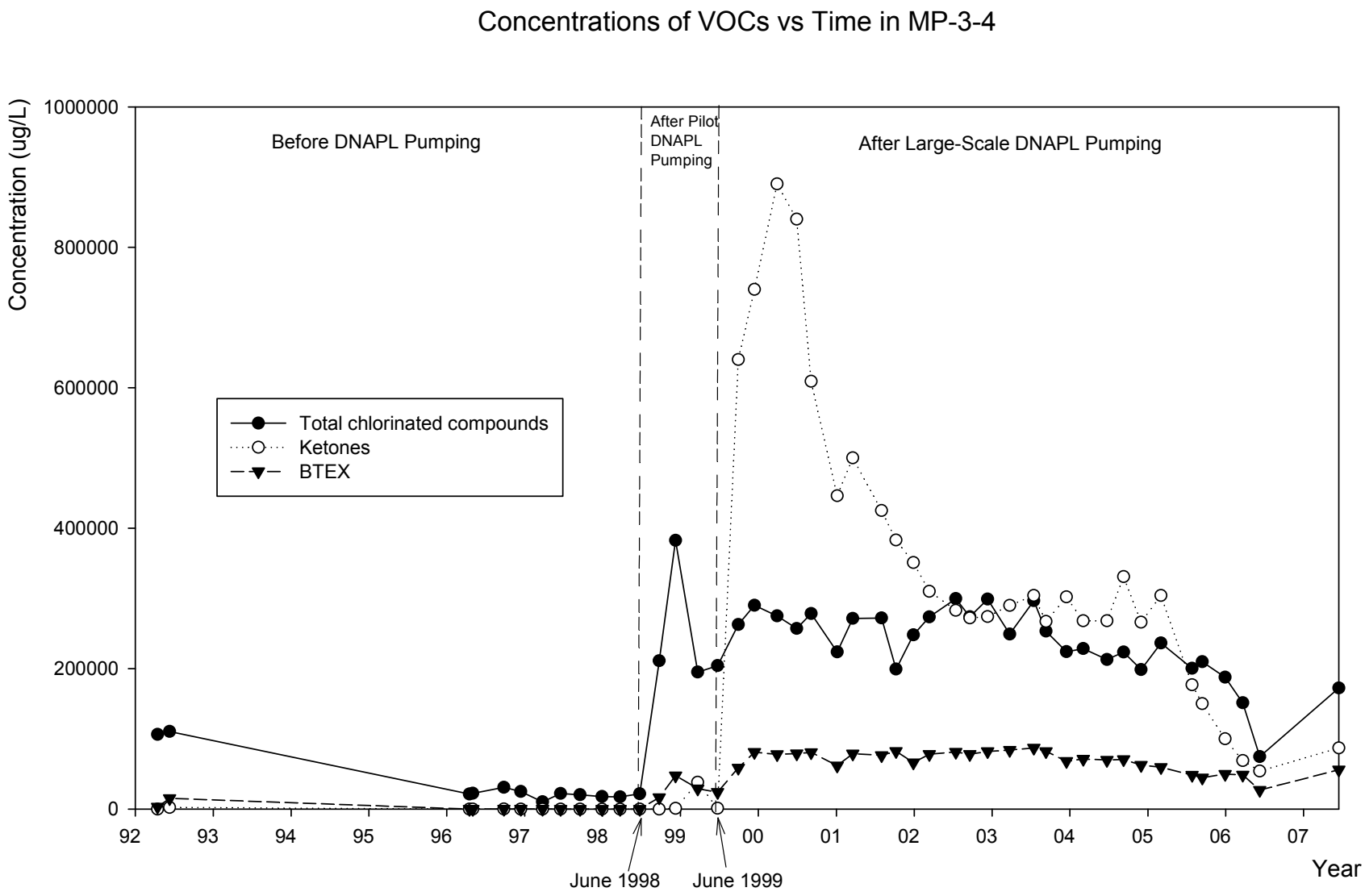


Figure 5.4 Concentrations of Chlorinated Compounds, BTEX, and Ketones in MP-3-4 from 1992 to 2007.
Well MP-3-4 is located near the source on the main groundwater flow direction.

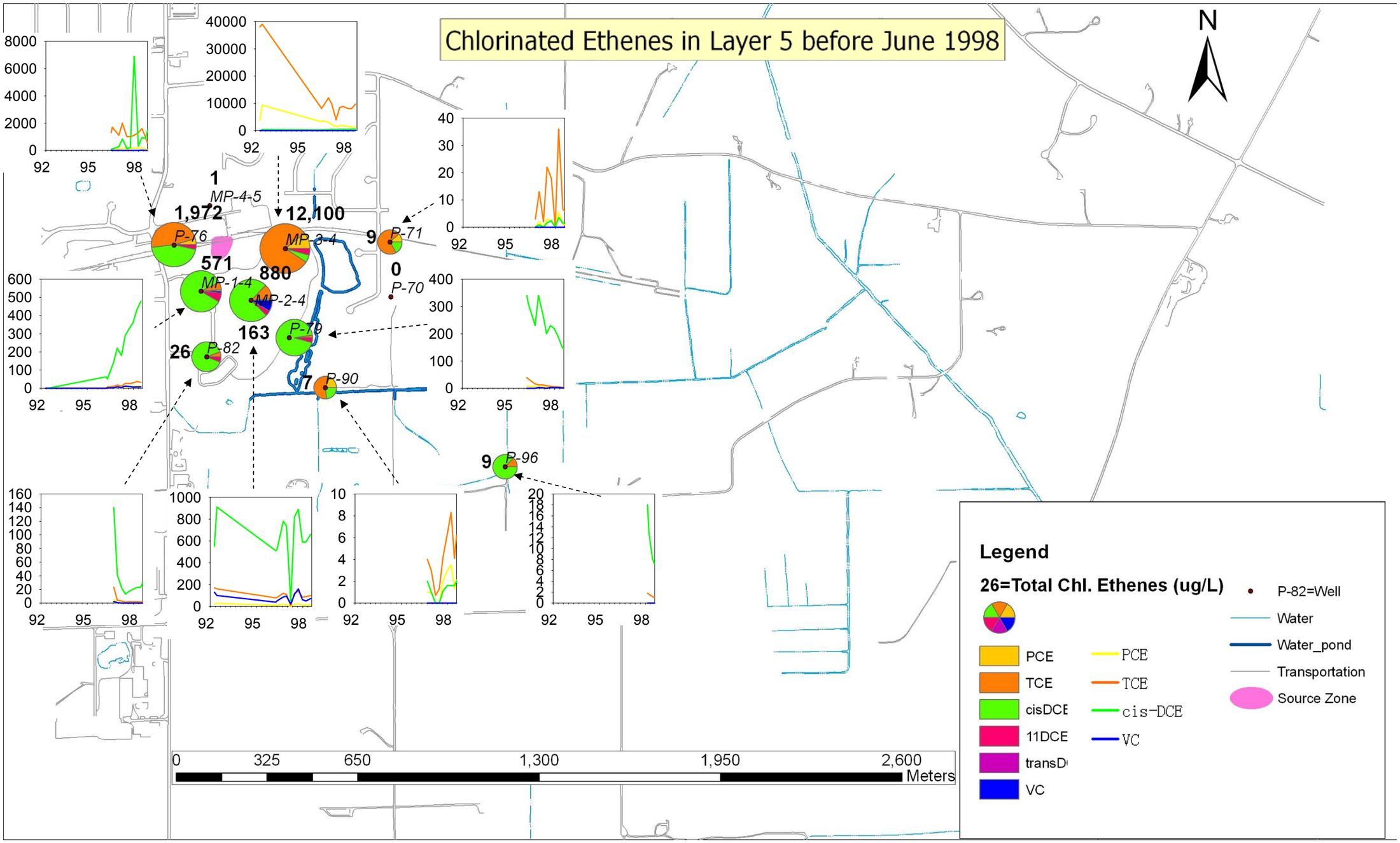


Figure 5.5 Chlorinated Ethenes in Layer 5 before June 1998
This is a plot showing composition of chlorinated ethenes in Layer 5 in June 1998 as well as chlorinated ethenes concentration time plots for each well during 1992 to June 1998.

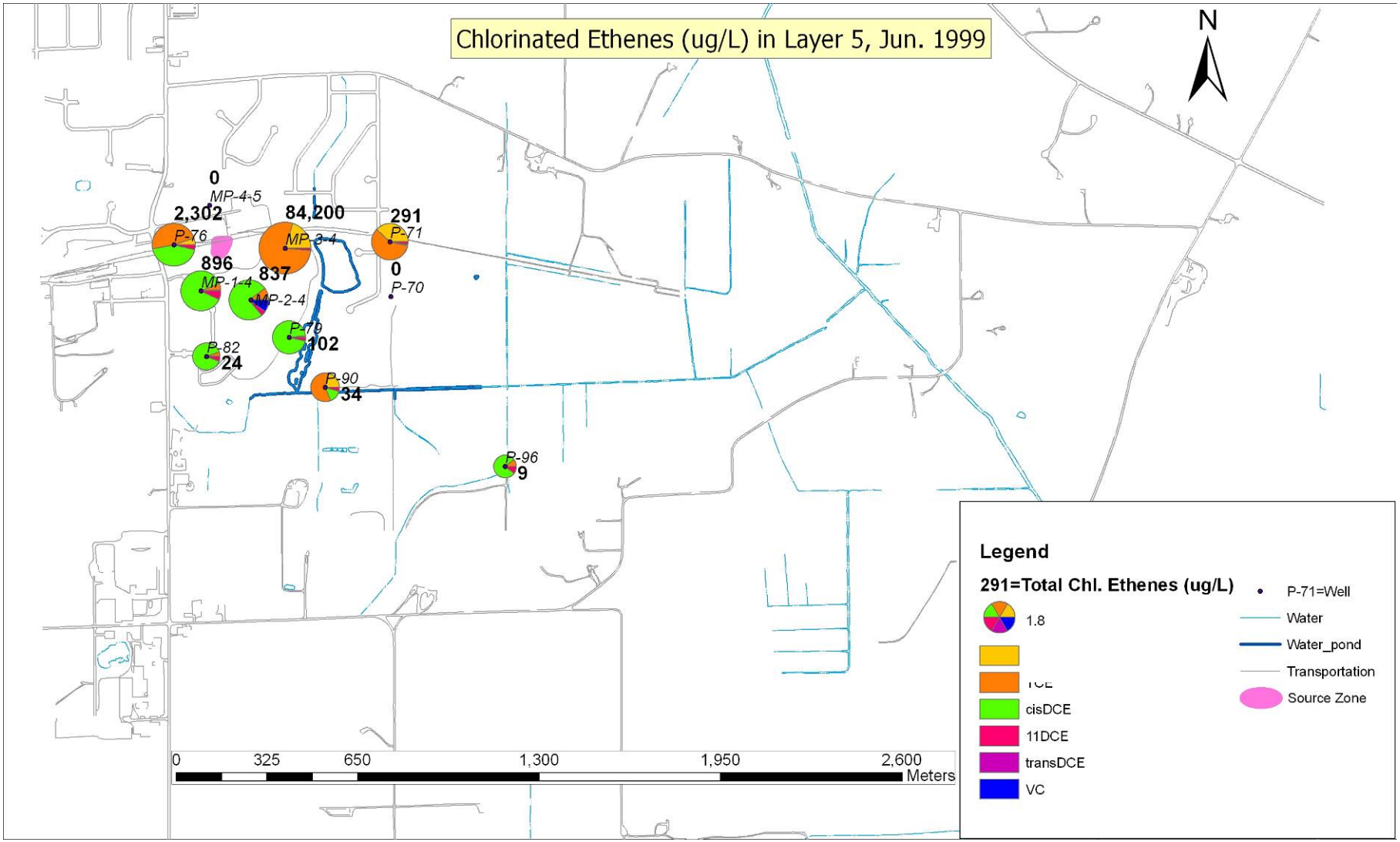


Figure 5.6 Chlorinated Ethenes in Layer 5 in June 1999

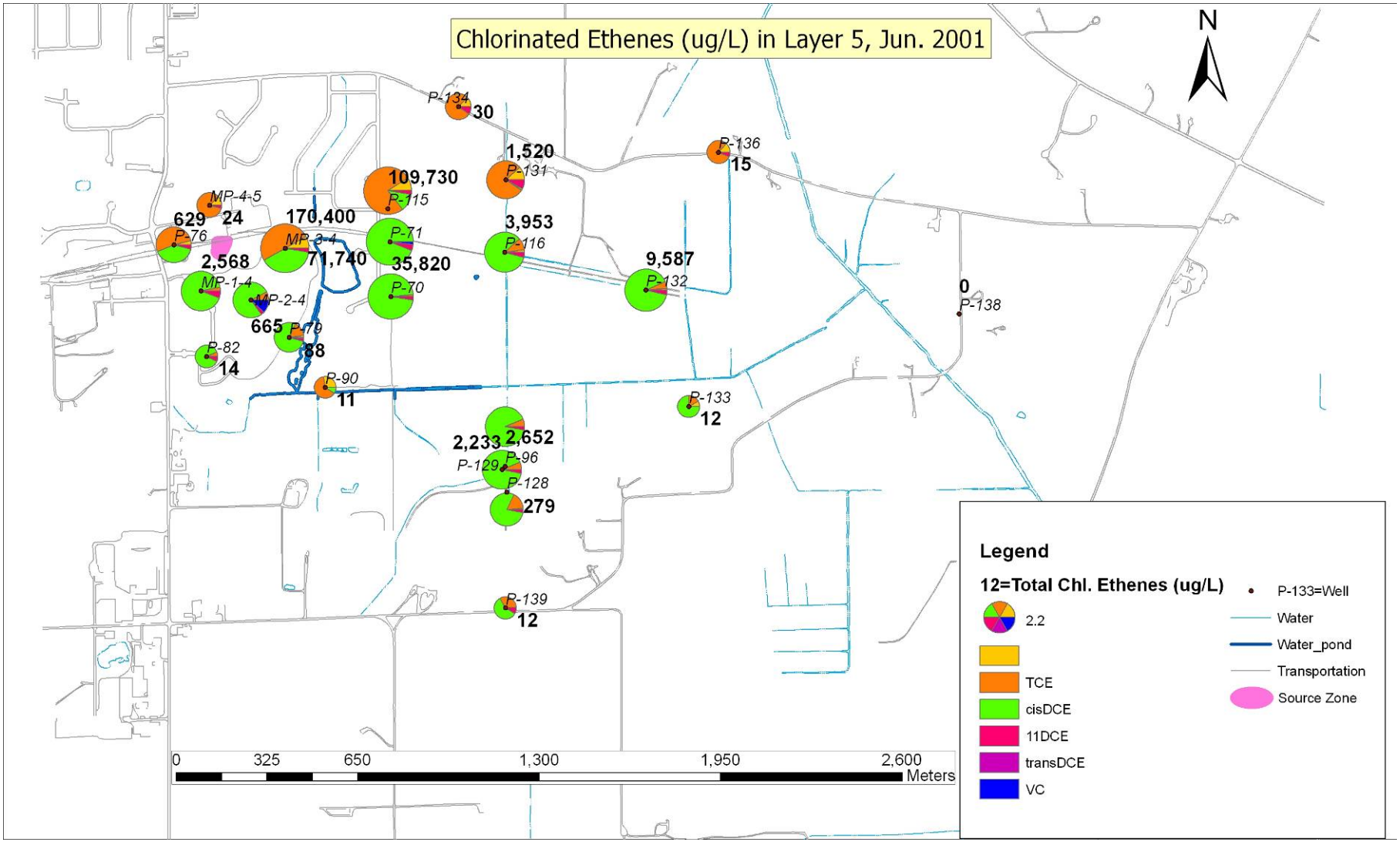


Figure 5.7 Chlorinated Ethenes in Layer 5 in June 2001

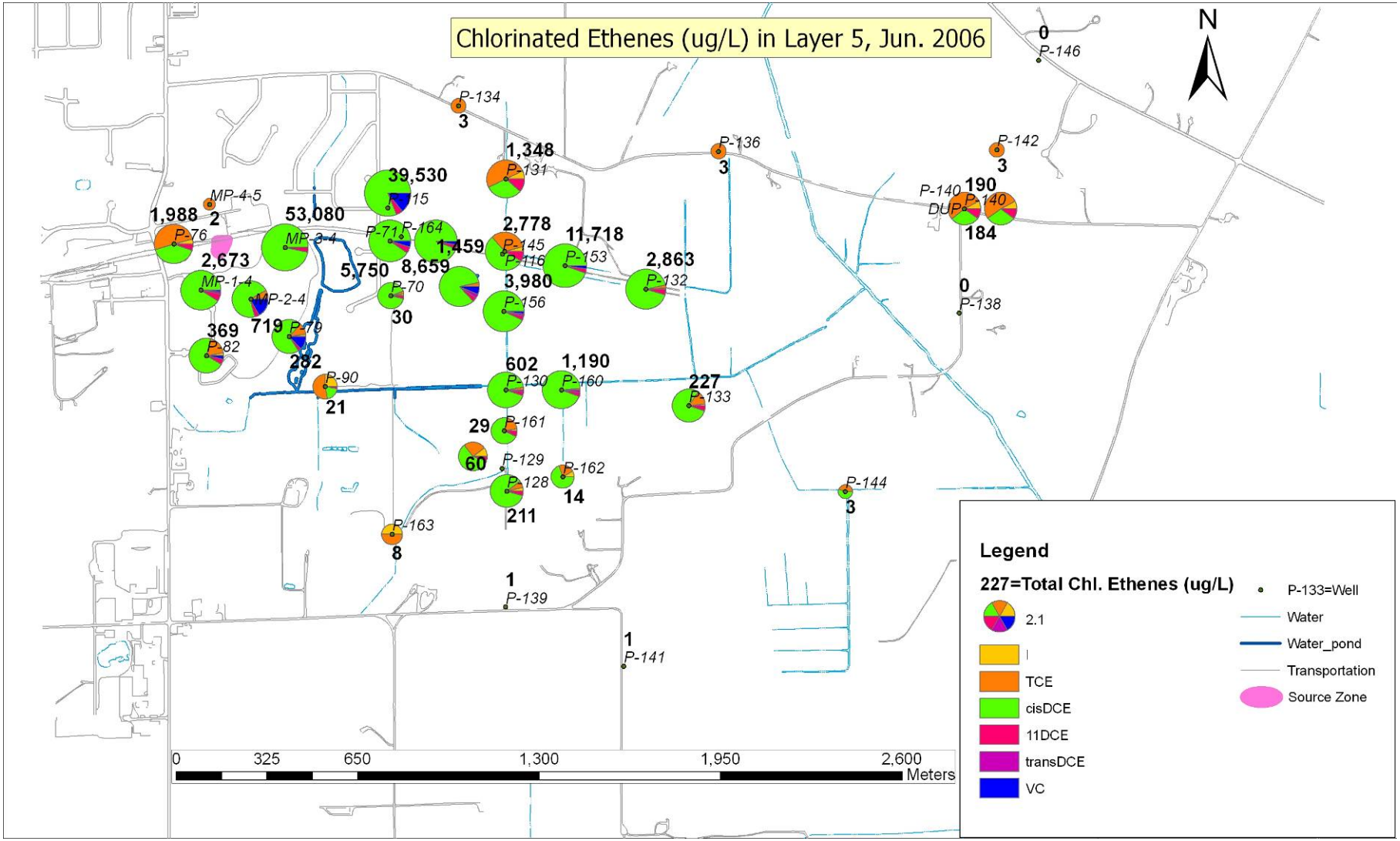


Figure 5.8 Chlorinated Ethenes in Layer 5 in June 2006

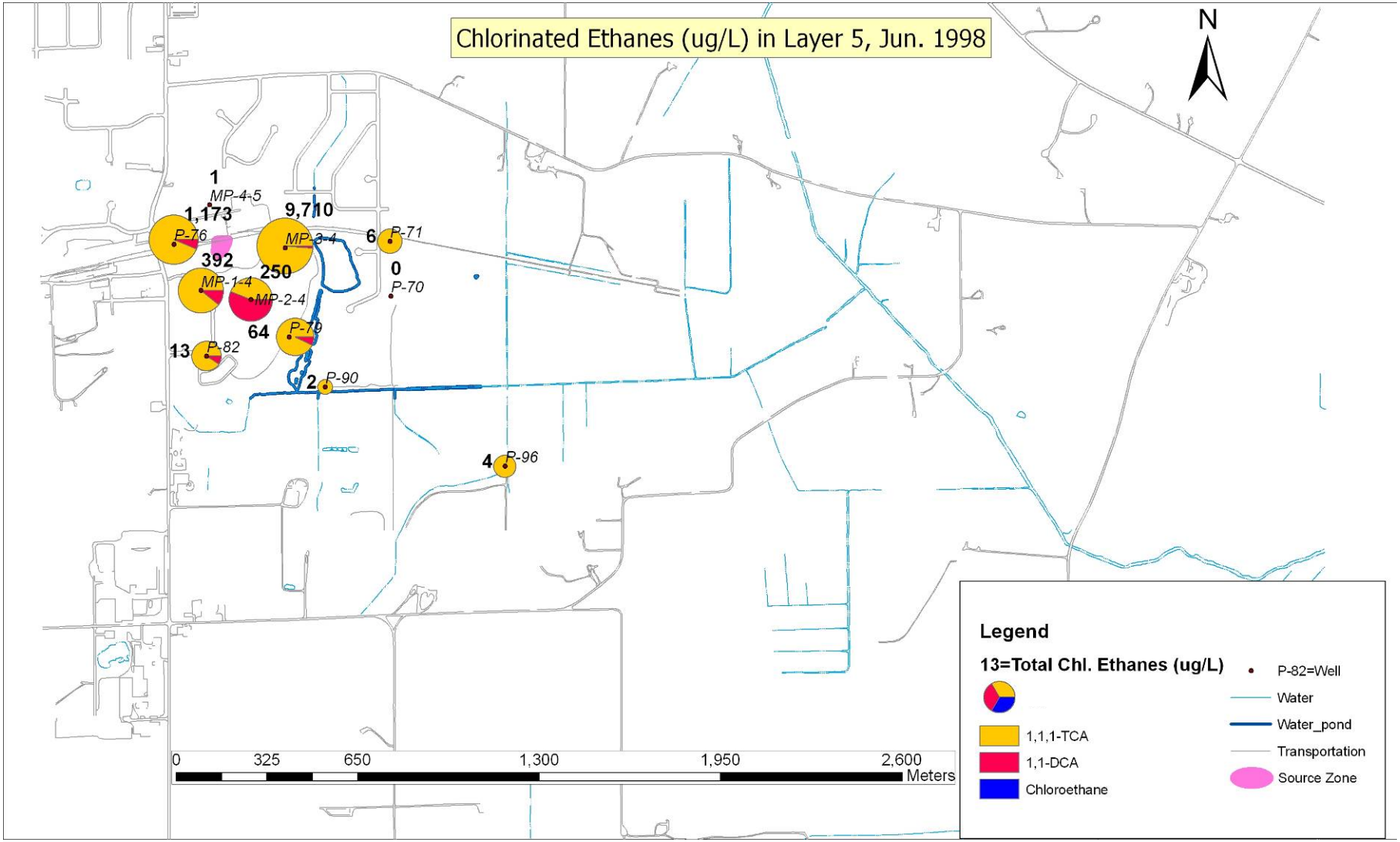


Figure 5.9 Chlorinated Ethanes in Layer 5 in June 1998

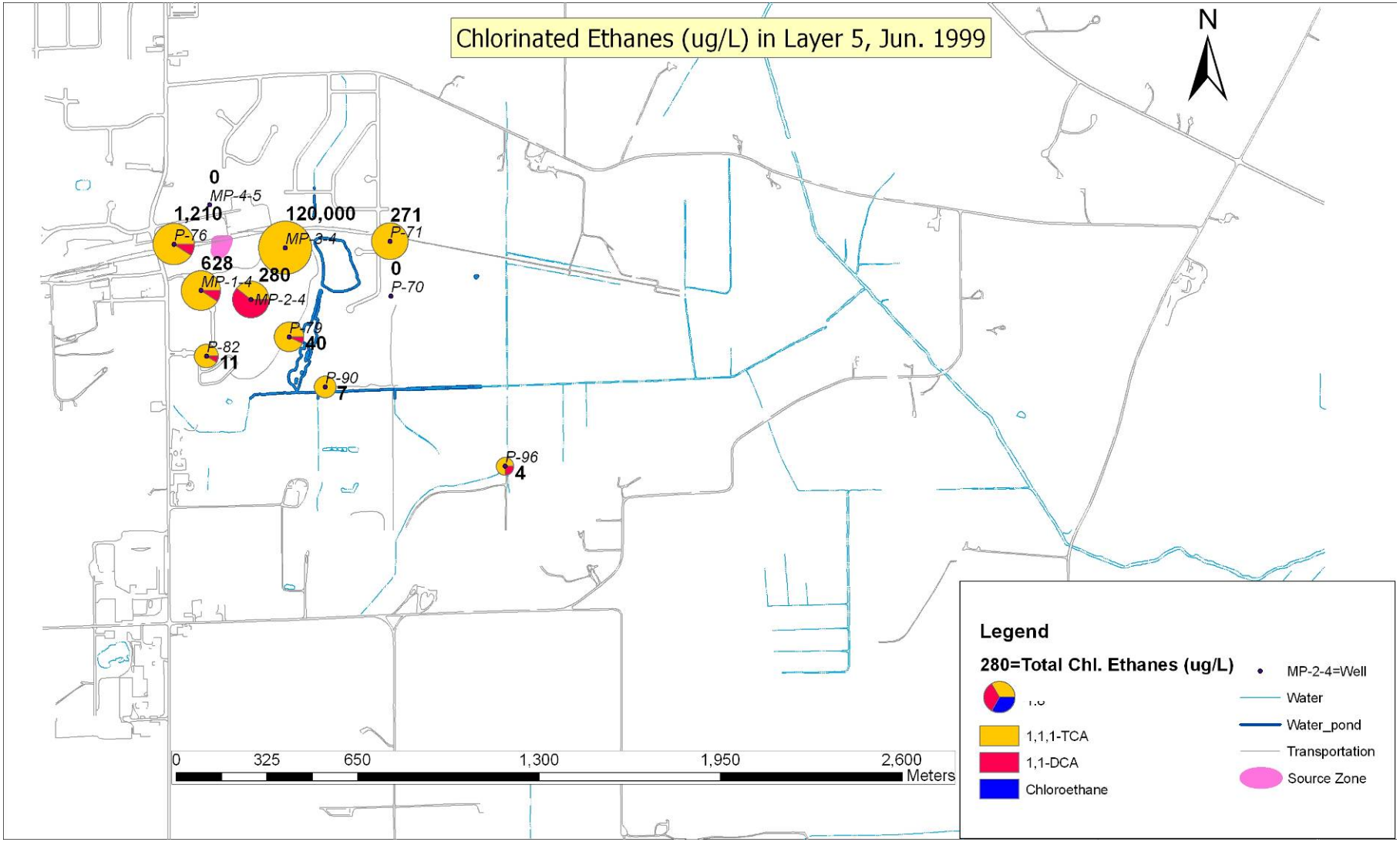


Figure 5.10 Chlorinated Ethanes in Layer 5 in June 1999

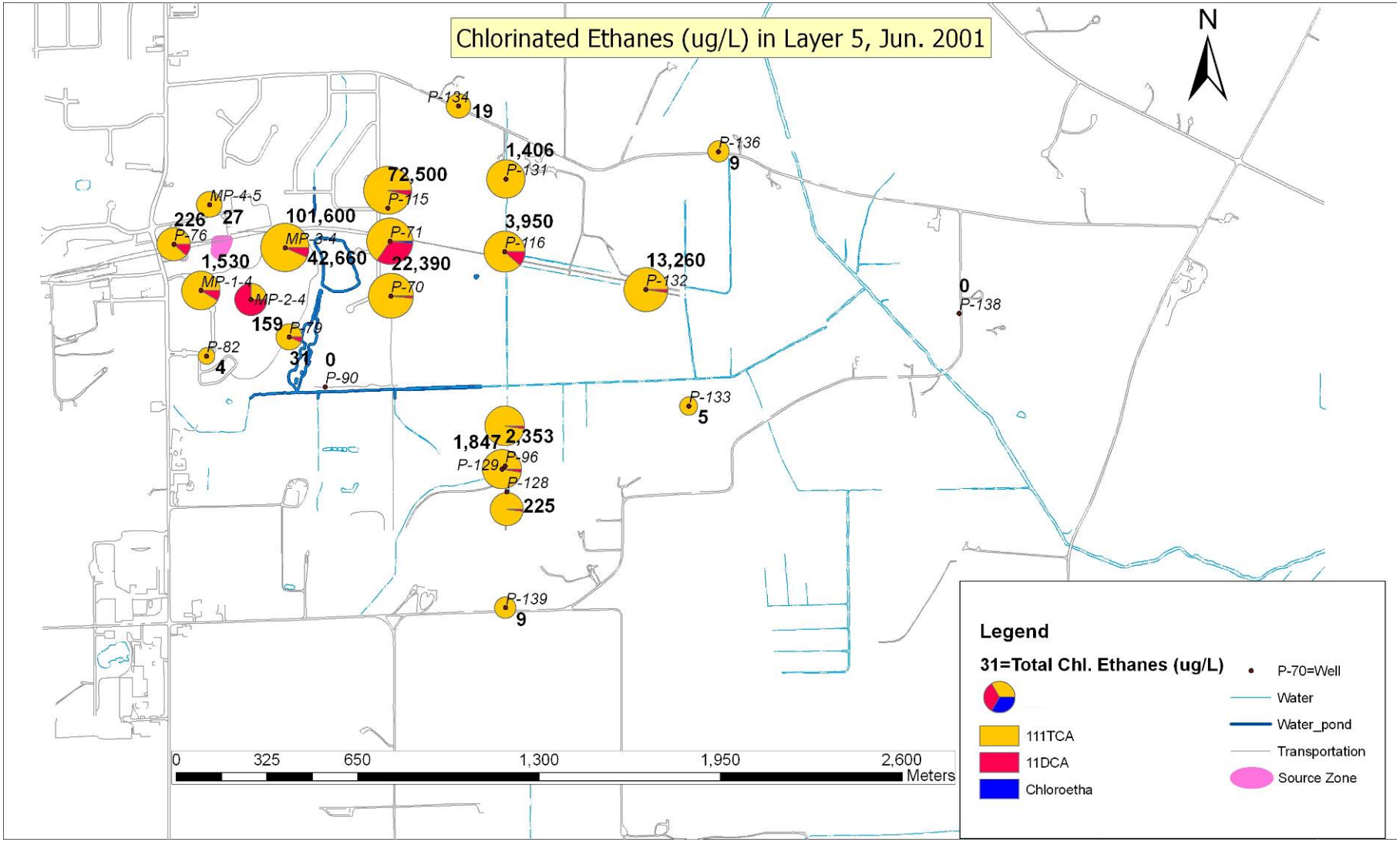


Figure 5.11 Chlorinated Ethanes in Layer 5 in June 2001

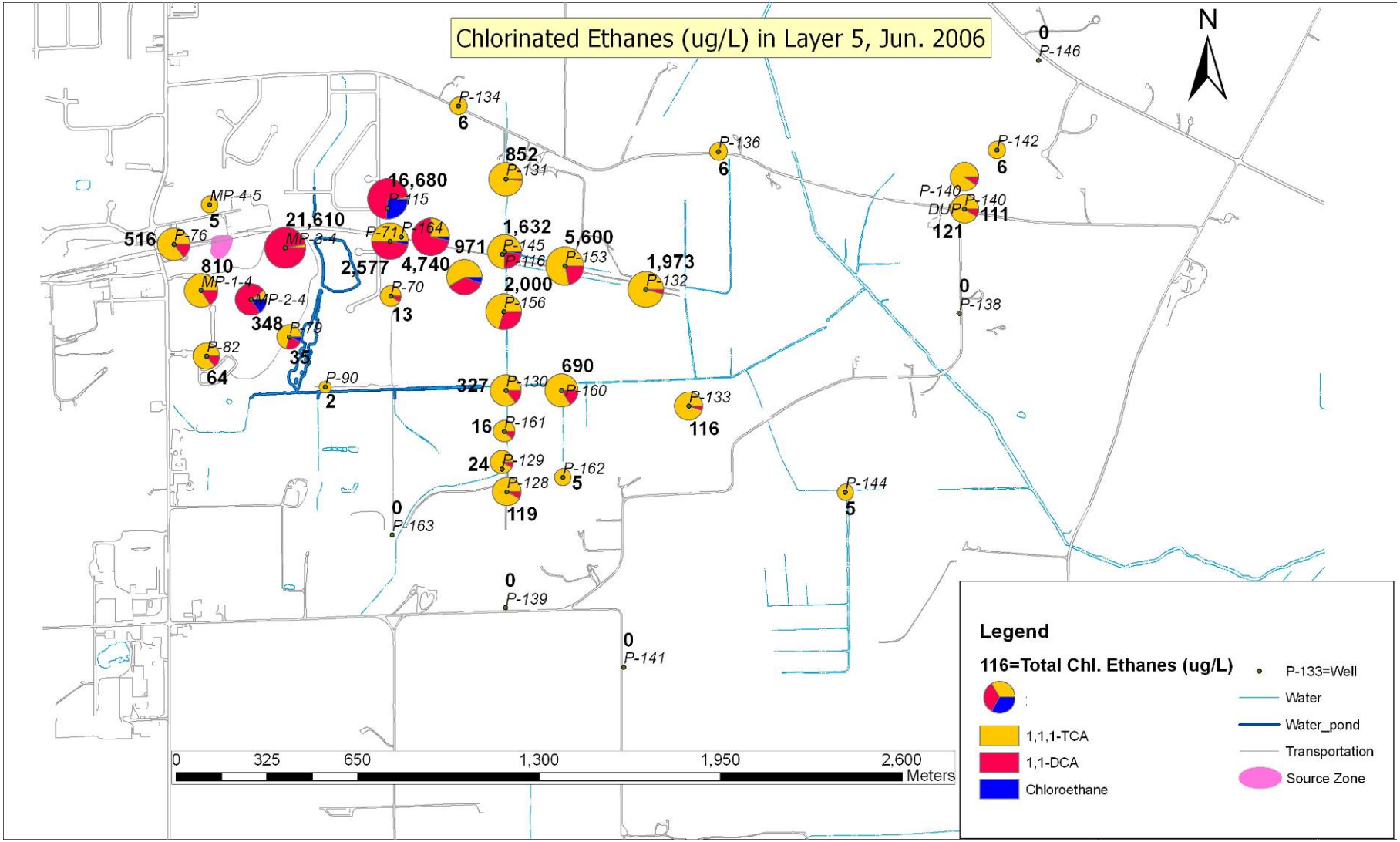


Figure 5.12 Chlorinated Ethanes in Layer 5 in June 2006

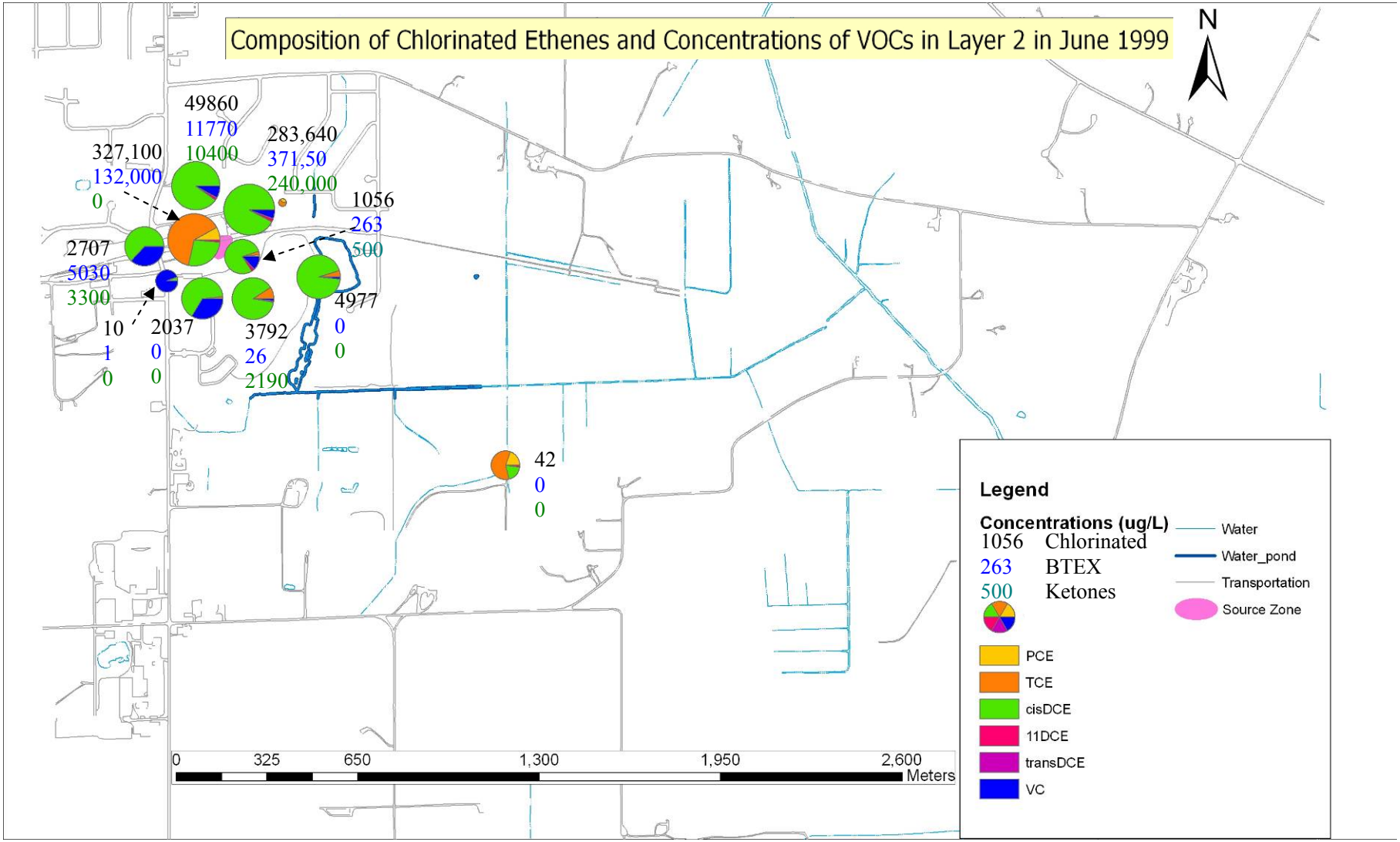


Figure 5.13 Composition of Chlorinated Ethenes and Concentrations of VOCs in Layer 2 in June 1999

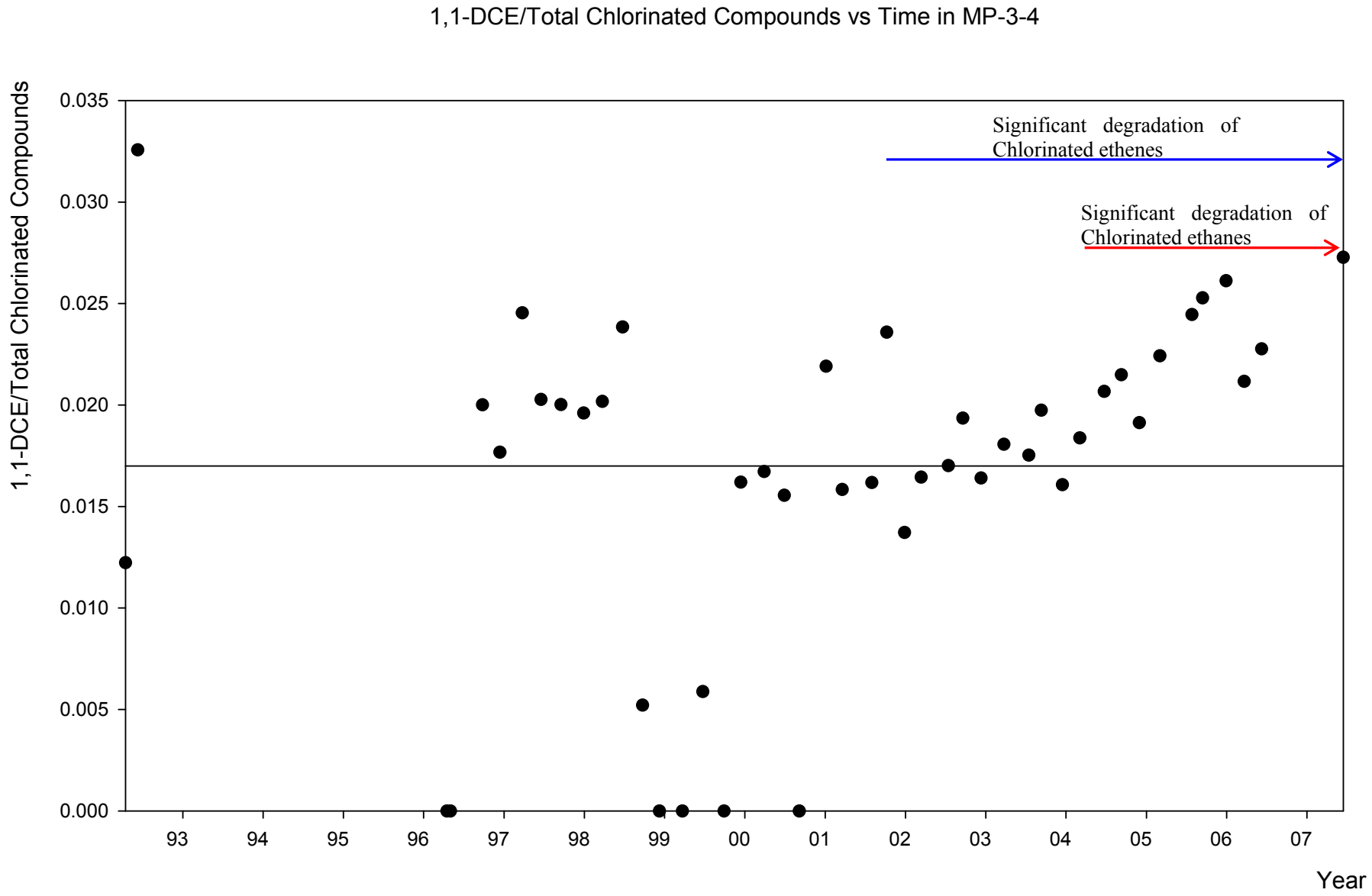


Figure 5.14 Percentage of 1,1-DCE out of the Total Chlorinated Compounds in MP-3-4 over Time.

5.2 Detailed sampling in September 2007

5.2.1 General Geochemistry

The concentrations of calcium and magnesium in Layer 5 ranged from 48.5 mg/L to 184 mg/L and 38.8 mg/L to 71.4 mg/L, respectively (Appendix II). The highest values were found near the source in well MP-3-4 (184 mg/L and 71.4 mg/L, respectively) and well P-115 (117 mg/L and 64.3 mg/L, respectively). Concentrations of sodium and potassium were generally low, with values ranging from 2.53 mg/L to 75.9 mg/L and 0.33 mg/L to 8.69 mg/L, respectively. The area near the source also had much higher sodium and potassium concentrations in the well MP-3-4. Concentrations of bicarbonate ranged from 174 mg/L to 236 mg/L, with the highest value found near the source in the well P-115. Concentrations of sulfate ranged from 0.25 mg/L to 19 mg/L, which were relatively low compared with the other species. The groundwater type in Layer 5 was generally determined to be calcium/magnesium-bicarbonate, with two exceptions, wells P-115 and MP-3-4, which had equal or more chloride than bicarbonate (Figure 5.15).

Chloride Concentration Chloride is one of the products of dechlorination of chlorinated compounds therefore it is possible to find a relationship between chloride and VOC concentration in groundwater with active biodegradation of chlorinated compounds. Concentrations of chloride ranged widely from 0.8 mg/L to 330 mg/L, with the highest values found near the source in the wells MP-3-4 and P-115. The distribution of chloride concentration (Figure 5.16) was very consistent with the distribution of concentrations of chlorinated ethenes or ethanes, which will be shown in section 5.2.3. Background chloride concentration seems to be around 15mg/L or 6.3mg/L in wells MP-6-25 or MP-6-27, both located upgradient of the plume. Even lower chloride concentrations such as 0.8, 2.9, and 4.6 mg/L can also be observed in some of the wells such as P-138, P-136,

and P-140 at the fringe of the plume (Figure 5.16), which had low contaminant concentrations and less extent of degradation (dechlorination) (which will be shown in section 5.2.3). The highest chloride concentrations were found near the source in well MP-3-4 and P-115 (Figure 5.16), which also had the highest total chlorinated compounds concentrations and greater extent of degradation (dechlorination). In the middle of the plume in the wells P-145, P-164, P-153, P-156, and P-116, chloride concentrations were in the range from 18 mg/L to 33mg/L, corresponding to moderate (lower than the area near the source but higher than the fringe of the plume) contaminant concentrations and extent of degradation.

The higher chloride concentrations found in the more contaminated areas were probably related to the dechlorination of chlorinated compounds. A positive relationship is observed between VOCs and chloride concentration (Figure 5.17). Moreover, the area near the source zone also had much higher concentrations of calcium, magnesium, sodium, potassium, and bicarbonate than the other areas. Those higher concentrations were probably related to carbonate mineral dissolution by CO_2, generated from mineralization of the organic contaminants.

Concentrations of geochemical parameters in selected sampling wells (Table 4-2) in other layers were also analyzed. Generally, the groundwater type was also calcium/magnesium-bicarbonate in most of these wells except that P-53 in Layer 2 and MP-3-1 in Layer 3, both at the same location as MP-3-4 in Layer 5 near the source zone, had relatively high calcium, magnesium, bicarbonate, and chloride concentrations and relatively low sulfate concentrations, similar to the geochemical constituents in MP-3-4 and P-115 in Layer 5. Again, these relatively higher ions concentrations indicate higher contaminant concentrations and/or higher degree of dechlorination in these wells. But

generally, the geochemistry in the other layers was less impacted by the contamination than in Layer 5.

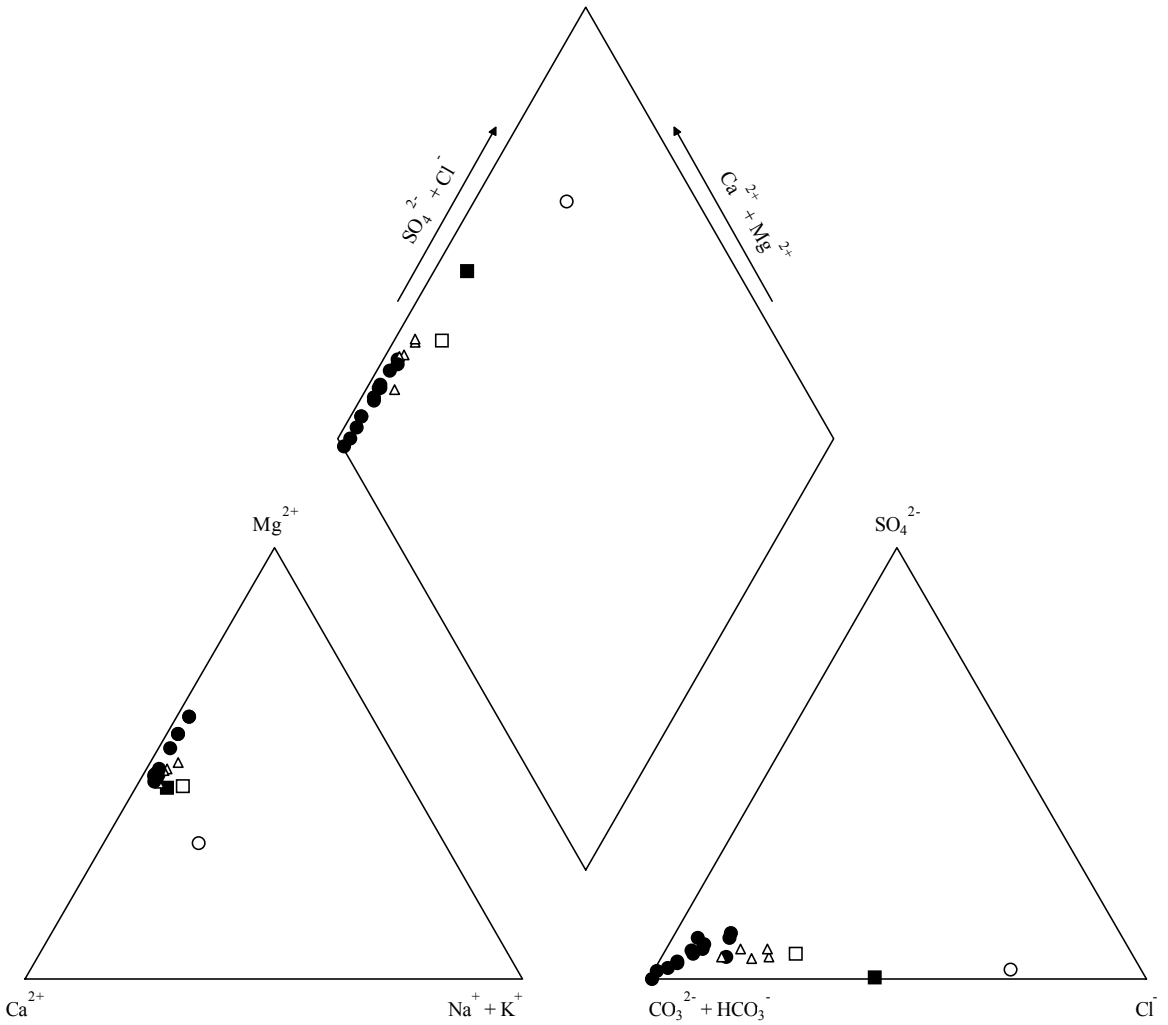


Figure 5.15 Piper Chart of the Groundwater in Layer 5
The open circle, filled-in square, and open square represent wells MP-3-4, P-115, and P-129, respectively. The open triangles represent wells P-145, P-164, P-153, P-156, and P-116.

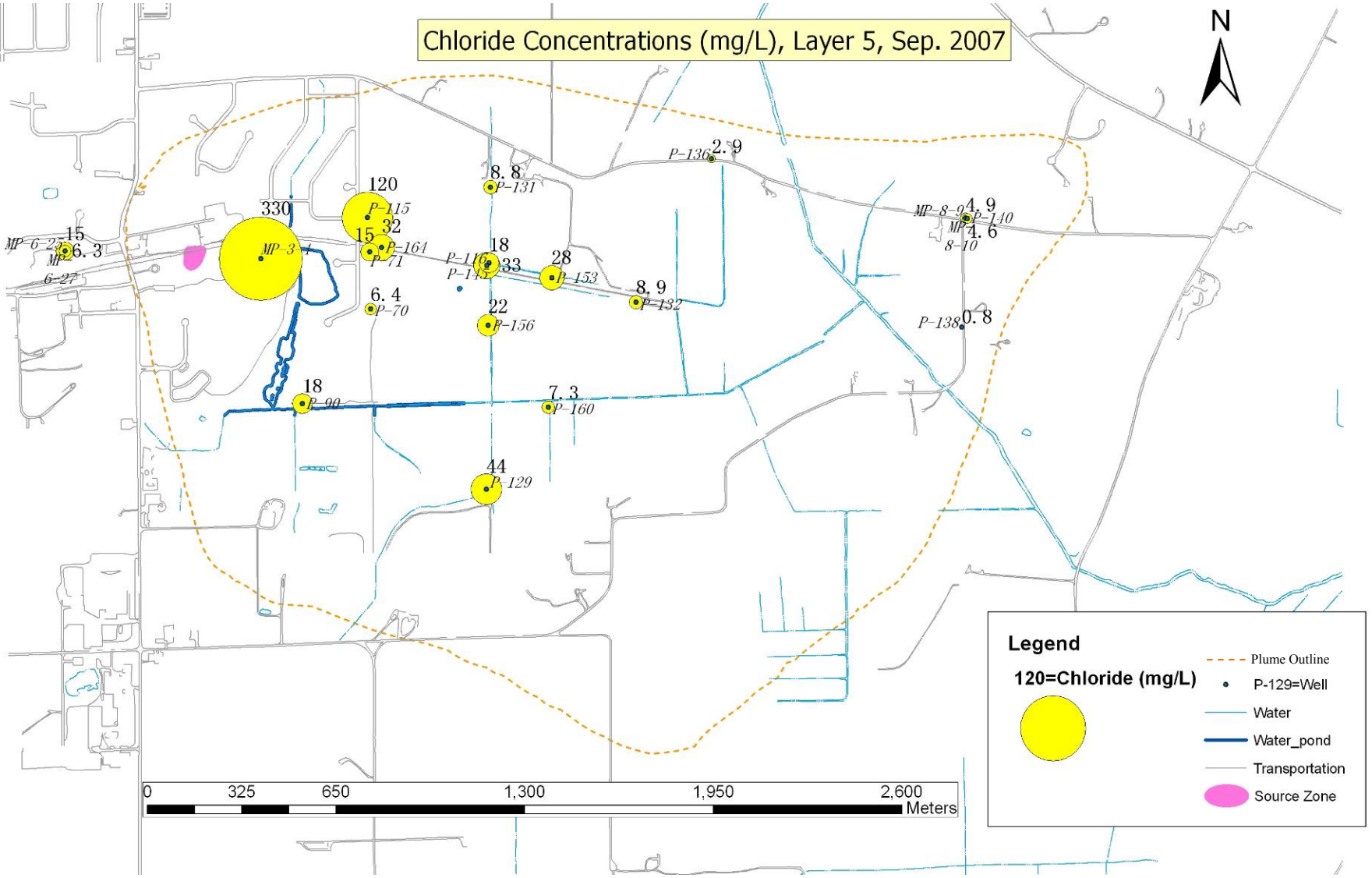


Figure 5.16 Chloride Concentrations in Layer 5, September 2007

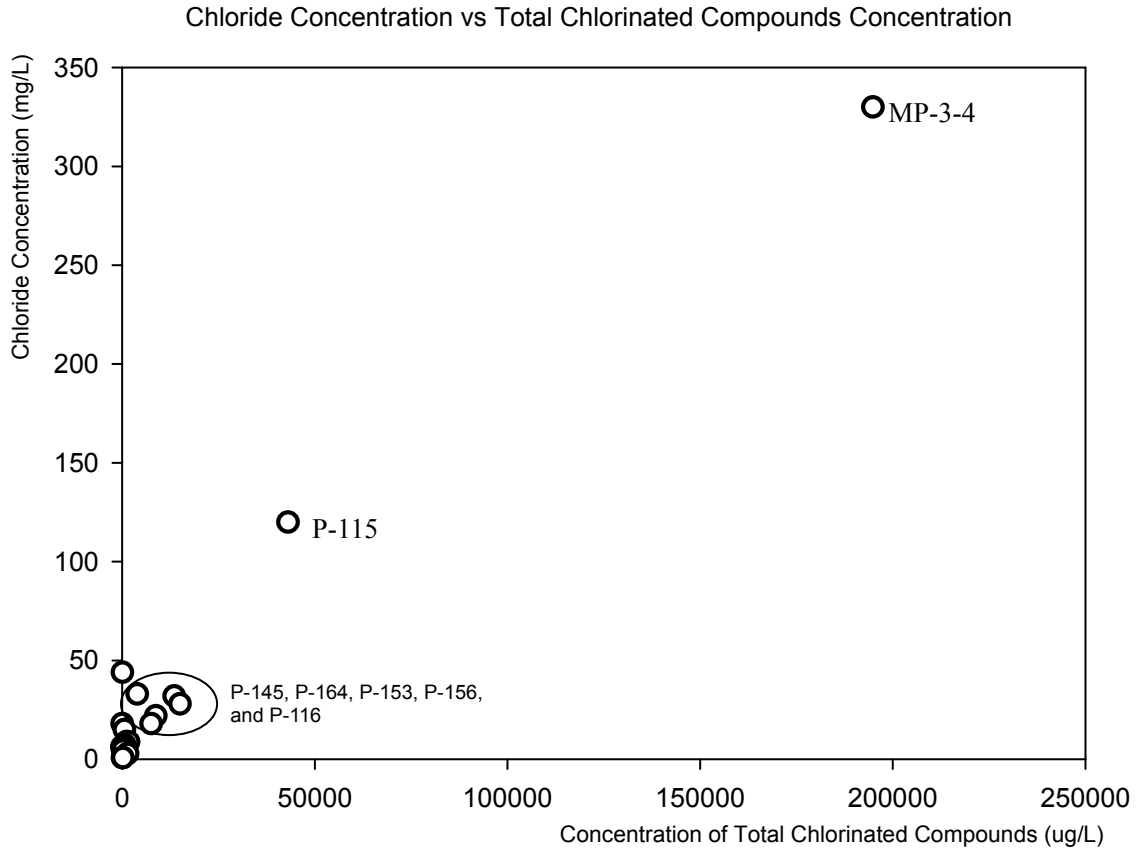


Figure 5.17 Chloride Concentration vs Total VOCs Concentration

5.2.2 Redox Conditions

Redox conditions in groundwater include aerobic, denitrification, manganese reducing, iron reducing, sulfate reducing and methanogenic conditions, from the most oxidative to the most reducing. In this study, the redox conditions are determined by redox-sensitive species including DO, Mn, Fe, SO_4^{2-} and methane. NO_3^- was not measured due to the very low background NO_3^- concentration.

The rule for determining the redox condition is that a high DO concentration (>1ppm) indicates aerobic conditions (Bjerg et al., 2003), a high manganese concentration indicates manganese reducing conditions, a high iron concentration indicates iron reducing conditions, a low sulfate concentration indicates sulfate reducing conditions, and a high methane concentration indicates methanogenic conditions, as stated in Section 1.2.1.

Dissolved oxygen (DO) concentrations in Layer 5 ranged from 0 to 8.3 ppm (Figure 5.18) (Appendix I). The area from the source zone to the middle of the plume, where wells MP-3-4, P-115, P-164, P-71, P-116, P-145, P-153, P-156, and P-160 were located, had DO concentrations ranging from 0 to 0.9 ppm and thus was determined to be under anaerobic conditions. The other plume area surrounding the anaerobic zone, where wells P-131, P-132, P-138, P-140, MP-8-10, P-70, P-90, P-129, and P-136 were located, had DO concentrations ranging from 3.4 ppm to 8.3 ppm and was determined to be under aerobic conditions.

Manganese concentrations in Layer 5 ranged from 0 to 1.46 mg/L (Figure 5.19) (Appendix II). The area from the source to the middle of the plume had manganese concentrations ranging from 0.17 mg/L to 1.46 mg/L in most of the wells except P-71 and P-116. The edge of the plume had almost nondetectable manganese concentration. A higher Manganese concentration represents a more reducing condition. Therefore, the

pattern of higher manganese concentrations in the area from the source to the middle of the plume was very consistent with the anaerobic and the aerobic zones determined by DO concentrations. The area near the source zone, which had the highest manganese concentrations (1.46 mg/L and 1.2 mg/L in wells MP-3-4 and P-115, respectively), and the center of the plume, which also had high manganese concentrations (0.76 mg/L and 0.53 mg/L in P-153 and P-156, respectively), were determined to be under at least manganese reducing conditions.

The iron concentrations in Layer 5 ranged from 0 to 51.8 mg/L (Figure 5.20) (Appendix II). The area near the source had extremely high iron concentrations in wells MP-3-4 and P-115 (51.8 mg/L and 18.3 mg/L, respectively), indicating at least iron reducing conditions in this area. The center of the plume had relatively low iron concentrations in wells P-153 and P-156 (2.1 mg/L and 1.9 mg/L respectively), compared to the highest values, indicating the absence of iron reducing conditions in this area.

The sulfate concentrations in Layer 5 ranged from 1 mg/L to 19 mg/L (Figure 5.21) (Appendix II), which were relatively low, compared to the other species. The background sulfate concentration was determined in well MP-6-29 (upgradient of the plume) to be between 16 mg/L to 19 mg/L. Concentrations in most of the areas were all only slightly lower than the background concentration, ranging from 9mg/L to 17mg/L. These concentrations indicated the absence of sulfate reducing conditions in these areas. Although sulfate concentrations in the area at the front of the plume were unexpectedly low (3 mg/L to 6 mg/L in wells P-138, P-136, and P-140), the area was determined to be under aerobic conditions based on DO values. Therefore, only the area near the source, which had a very low sulfate concentration of 1mg/L in well P-115, was determined to be under at least sulfate reducing condition.

Methane concentrations in Layer 5 ranged from 0 to 959 μ g/L, which seemed to be relatively low, probably indicating the absence of methanogenic conditions in the whole plume area (Figure 5.22) (Appendix III). The highest values were observed nearest to the source in well MP-3-4 (894 μ g/L) and in the center of the plume in well P-156 (959 μ g/L), which were consistent with the most reducing conditions determined by DO, manganese, iron, and sulfate concentrations in these areas.

In summary, the whole plume area in Layer 5 can be divided into an aerobic zone at the edge (approximately 5/6 of the total area) and an anaerobic zone from the source to the middle (approximately 1/6 of the total area) (Figure 5.23). Within the anaerobic area, the area near the source was determined to be under sulfate reducing and iron reducing conditions and the center of the plume was determined to be under manganese reducing conditions.

Redox conditions generally became less and less reducing further away from the source (Figure 5.23). However, the area nearest to the source (iron reducing in MP-3-4) had a less reducing condition than the area further to the east (sulfate reducing in P-115). This pattern may be related to the higher proportion of ketones in the area further to the east, which will be explained in the next section on VOCs. The redox conditions in the area surrounded by wells P-164, P-71, P-145, and P-116 upgradient to the center of the plume, seemed to be affected by the groundwater extraction in wells P-164 and P-145 of the Hydraulic Barrier System, which could have caused more oxidative groundwater from the edge of the plume to move towards this area. Otherwise, the redox conditions in this area should be more reducing, likely to be between sulfate reducing to manganese reducing according to the redox conditions in upgradient (sulfate reducing) and downgradient (manganese reducing).

As a whole, the redox conditions within the plume area in Layer 5 were not very reducing. The majority of the aquifer (5/6) was under aerobic condition and only a very small part of the aquifer was more than iron reducing. According to Bradley (2000), at least iron reducing condition is required for reductive dechlorination of TCE to cis-DCE. Therefore, reductive dechlorination of TCE to cis-DCE could only occur in the part of the aquifer near the source zone in Layer 5.

On the other hand, in Layer 2, the area near the source had an extremely high iron concentration (259 mg/L) and a very low sulfate concentration (0.25 mg/L) in well P-53. Large amounts of VC and ethene were also present. Thus, the redox condition in the area near the source in Layer 2 was determined to methanogenic condition, which was more reducing than the redox conditions in Layer 5. Redox conditions determined in selected wells in the other layers were generally aerobic to slightly anaerobic except that MP-3-1 in Layer 3, at the same location as MP-3-4 near the source, seemed to be also under methanogenic reducing conditions and MP-3-2 in Layer 4 seemed to be under manganese to iron reducing conditions.

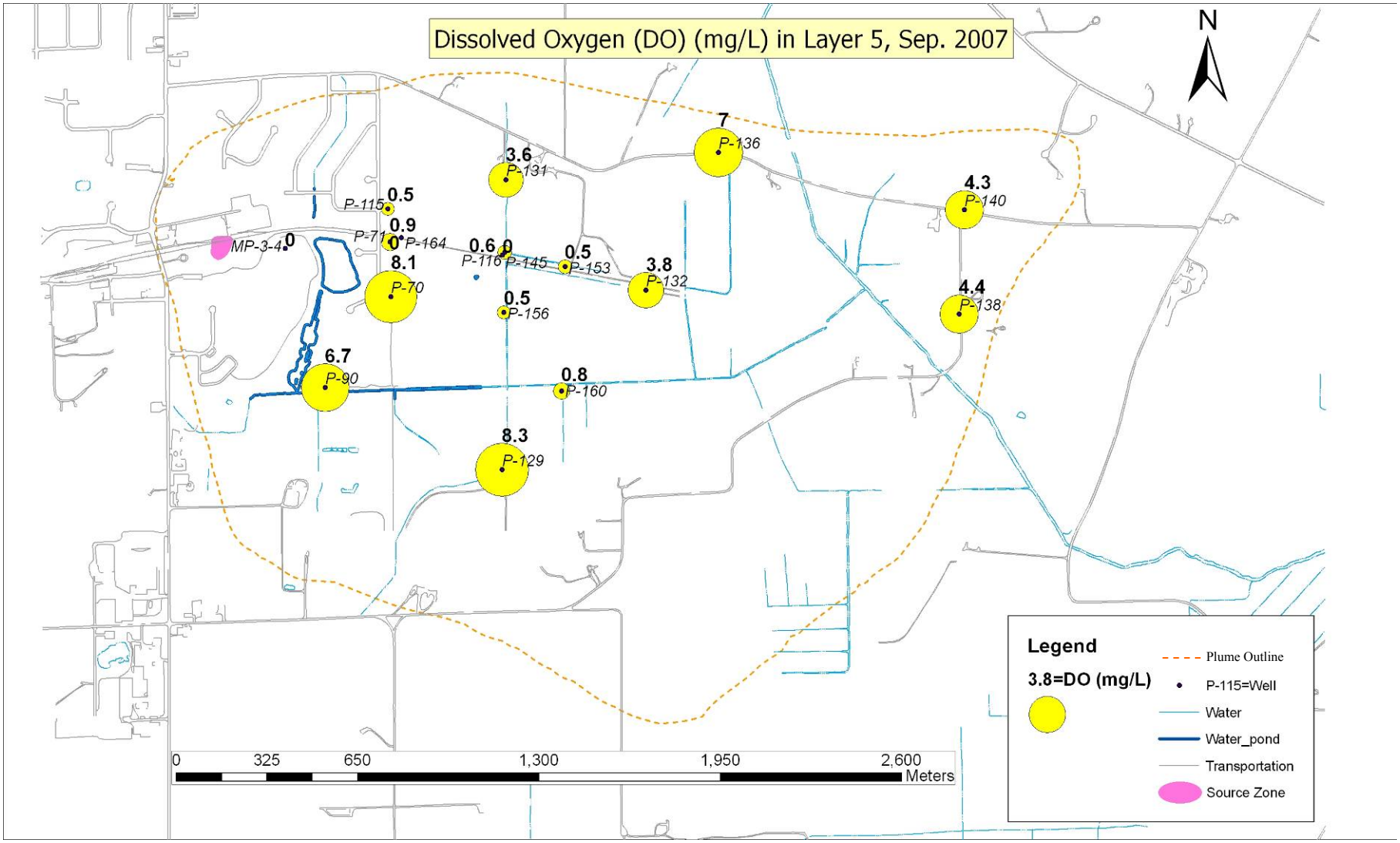


Figure 5.18 Dissolved Oxygen (DO) in Layer 5 in September 2007

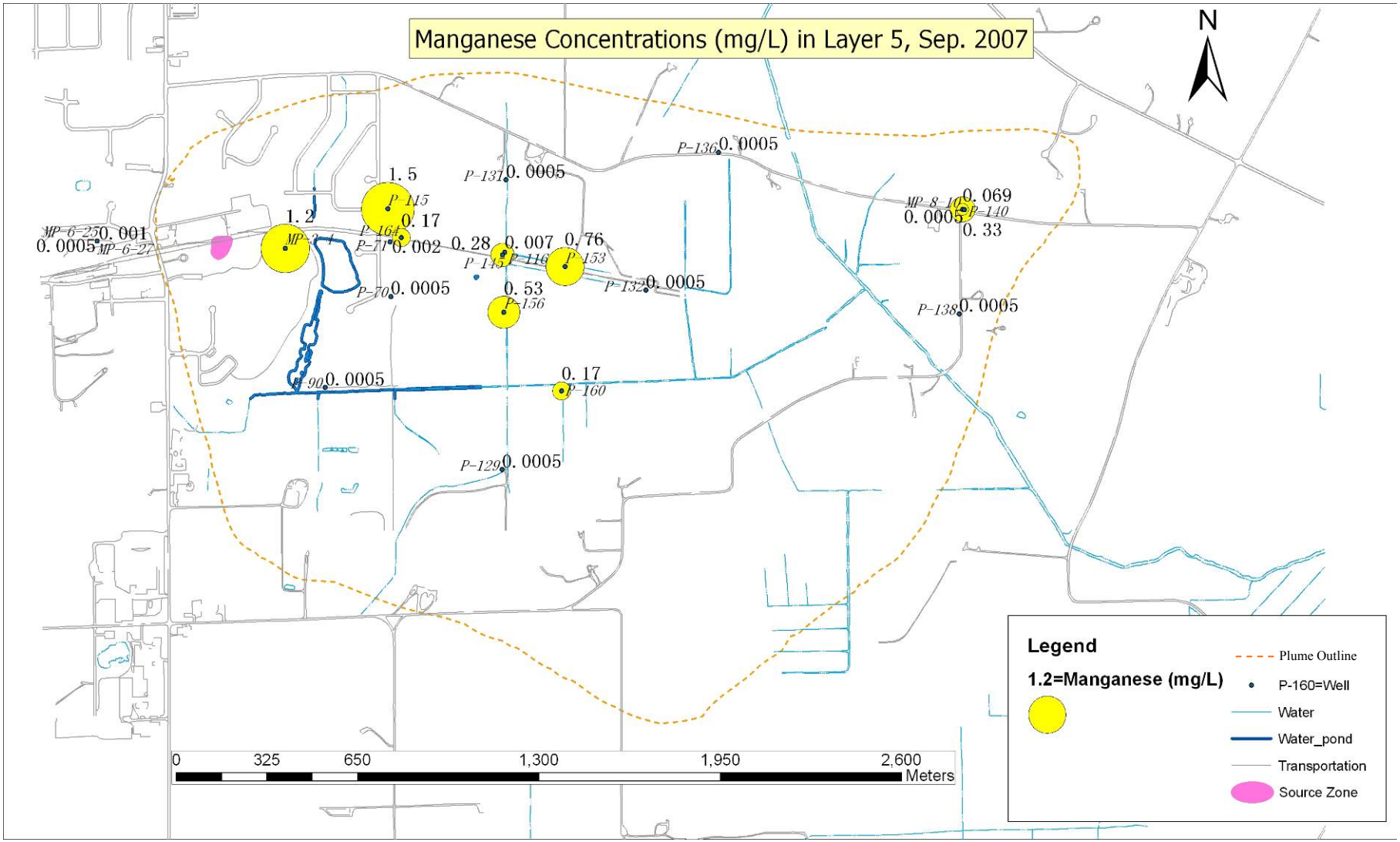


Figure 5.19 Manganese Concentration (mg/L) in Layer 5 in September 2007

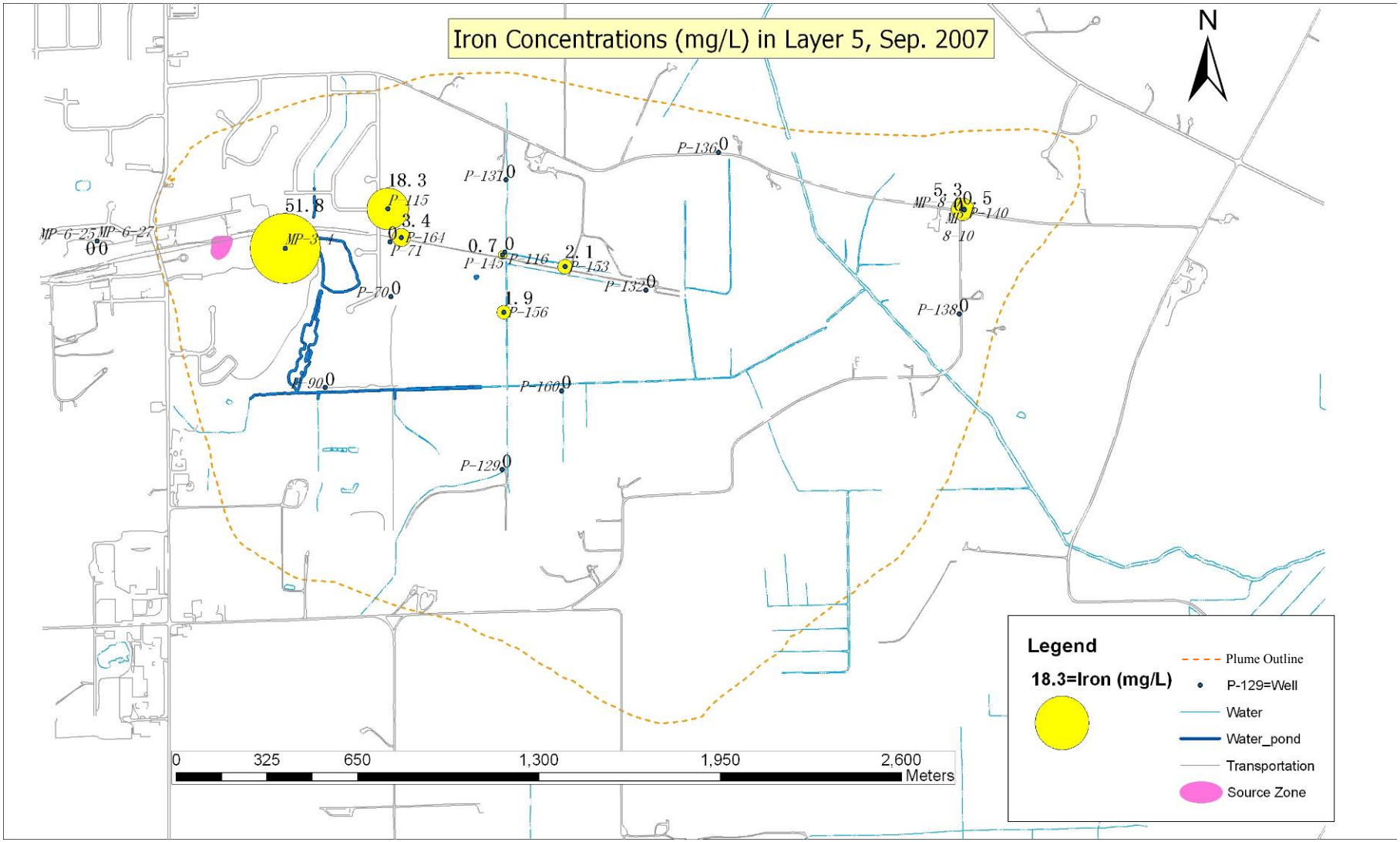


Figure 5.20 Iron Concentration (mg/L) in Layer 5 in September 2007

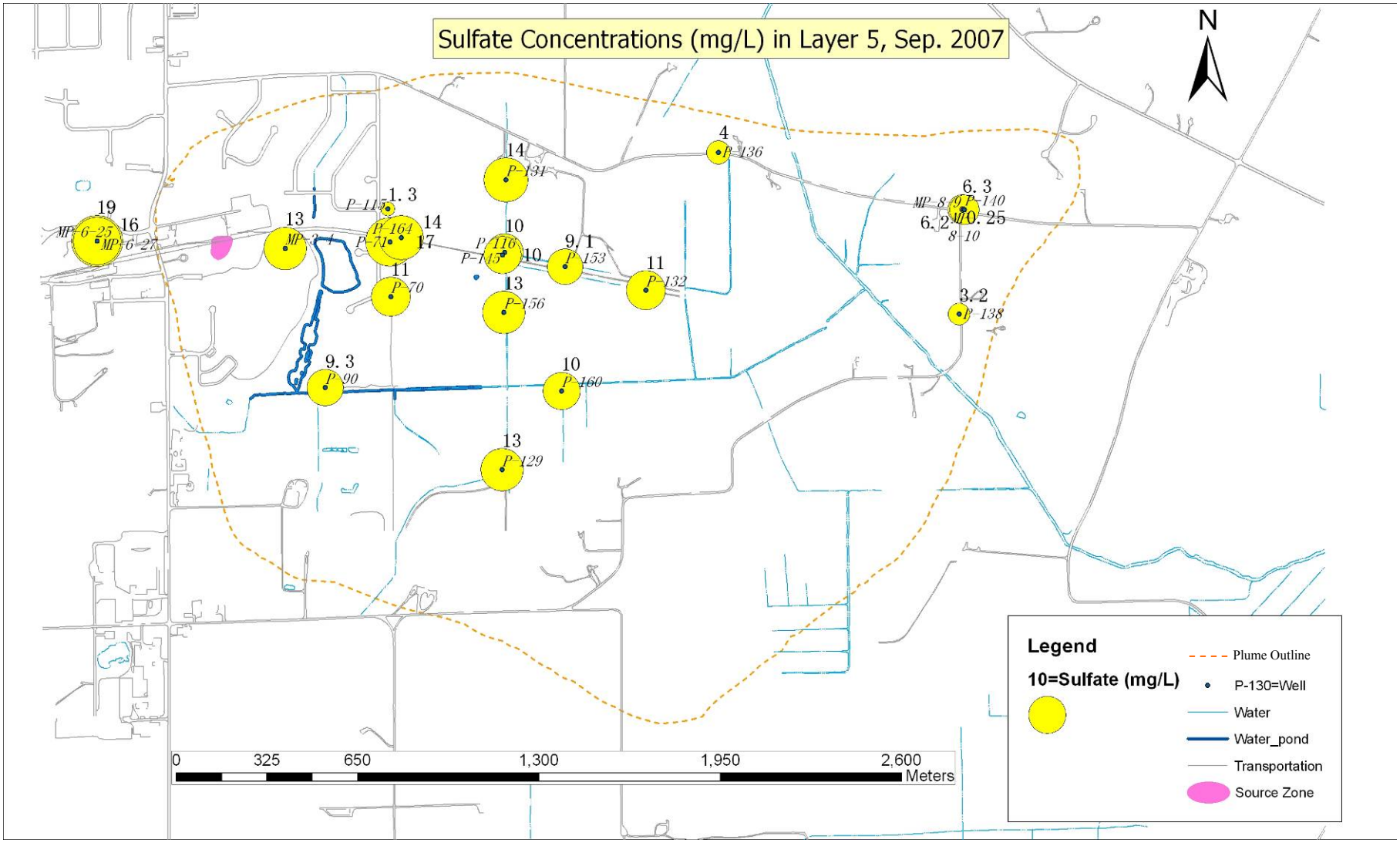


Figure 5.21 Sulfate Concentration (mg/L) in Layer 5 in September 2007

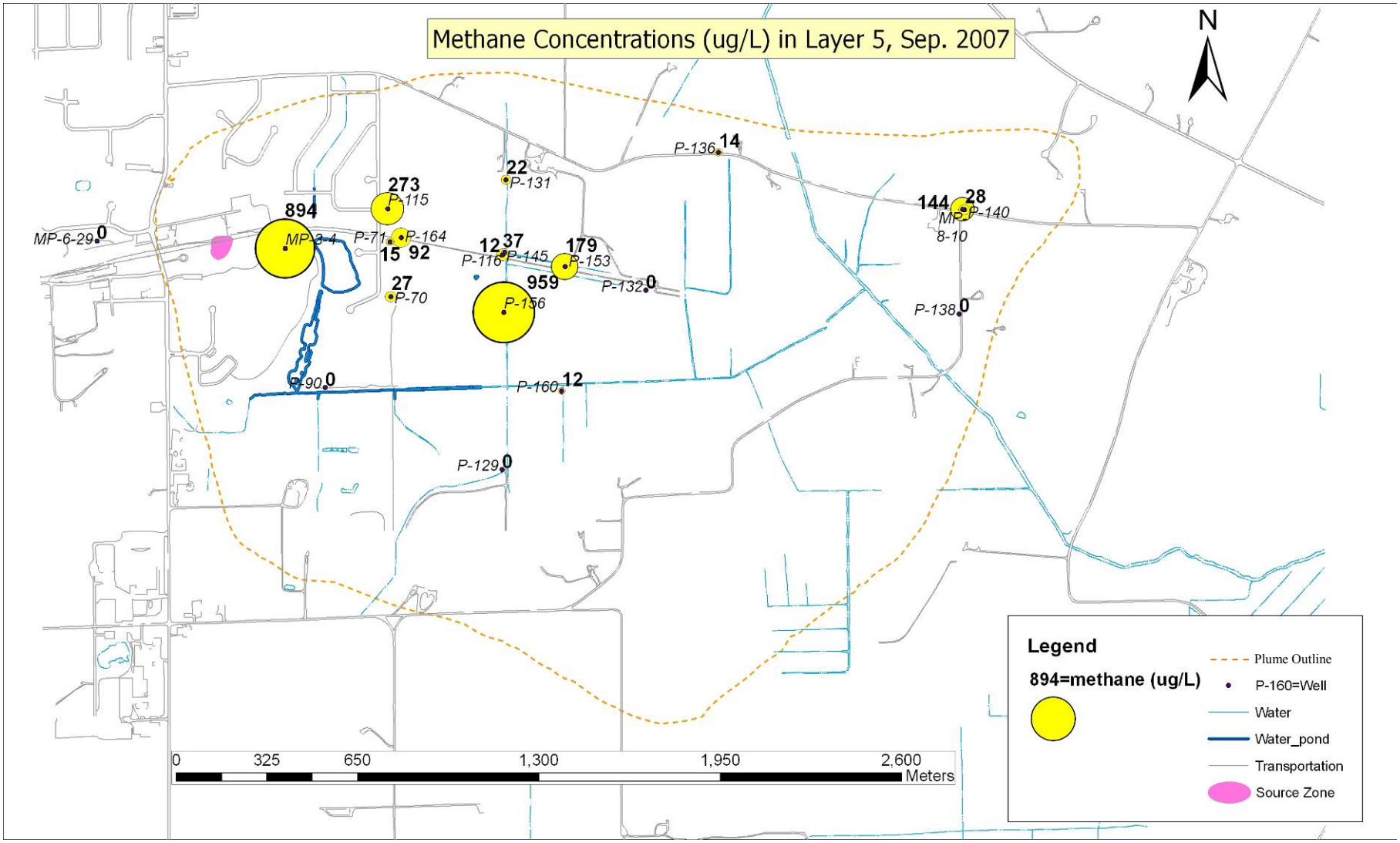


Figure 5.22 Methane Concentration (μ g/L) in Layer 5 in September 2007

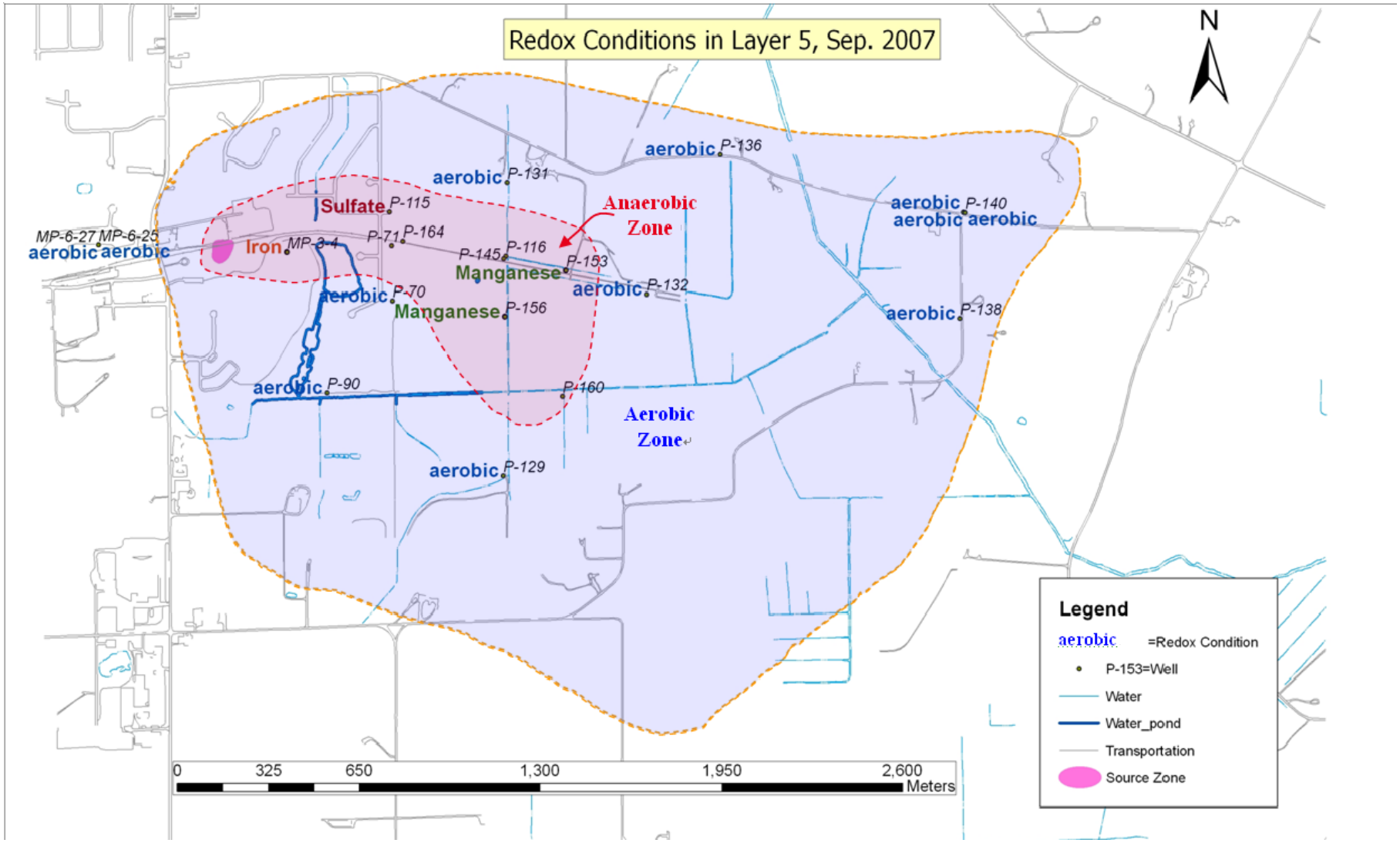


Figure 5.23 Redox Conditions in Layer 5 in September 2007

The whole plume area in Layer 5 can be divided into an aerobic zone (approximately 5/6 of the total area) and an anaerobic zone from the source to the middle (approximately 1/6 of the total area), based on redox sensitive species. Within the anaerobic area, the area near the source was determined to be under sulfate reducing and iron reducing conditions and the center of the plume was determined to be under manganese reducing conditions. Redox conditions generally became less reducing further away from the source.

5.2.3 VOCs and Dissolved Gases

The concentration of total VOCs in Layer 5 ranged from 6 μ g/L to 335,940 μ g/L, with the highest concentrations found near the source in wells MP-3-4 (335,940 μ g/L) and P-115 (43,060 μ g/L) (Figure 5.24) (Appendix IV). The center of the plume also had high concentrations in wells P-153 (15,020 μ g/L) and P-156 (8,755 μ g/L). The concentrations generally decreased along the flow path from west to the east and from the middle to the edge of the plume, with the exception of the area surrounded by wells P-71 (609 μ g/L), P-116 (7,511 μ g/L) and P-145 (3,967 μ g/L), which had lower concentrations than the downgradient area (the center of the plume), where wells P-153 (15,020 μ g/L) and P-156 (8,755 μ g/L) were located (Figure 5.24). These lower concentrations were likely caused by groundwater extraction within P-164 and P-145 of the Hydraulic Barrier System starting from 2003.

The BTEX concentration and total ketones concentration in Layer 5 were much higher near the source zone in well MP-3-4 (59,100 and 82,000 μ g/L, respectively) and well P-115 (13,070 and 65,000 μ g/L, respectively) (Figure 5.24) (Appendix IV). The areas further away all had BTEX concentrations below 221 μ g/L and nondetectable ketones concentrations. The much higher concentrations near the source were consistent with the most reducing redox conditions in this area (determined in the previous section), due to the contribution of BTEX and ketones as electron donors. The plumes of BTEX and ketones were much shorter than the plume of chlorinated compounds, probably due to faster degradation of BTEX and ketones. It was noted that the area further to the east had a higher proportion of ketones out of total VOCs in P-115 than the area nearest to the source in well MP-3-4 (Figure 5.24). This higher proportion might have caused the more

reducing condition in the area further to the east (sulfate reducing) than the area nearest to the source, because ketones are stronger electron donors, compared to BTEX.

Chlorinated Ethenes The PCE and TCE concentrations in Layer 5 were below 1,000 μg/L in all the wells. The highest PCE concentration was observed near the source in well MP-3-4 (977 μg/L), while the highest TCE concentration was found in the middle of the plume in wells P-116 (703 μg/L) and P-131 (486 μg/L) (Appendix IV).

The cis-DCE concentrations in Layer 5 ranged from 0 to 110,000 μg/L, which were much higher than the PCE and TCE concentrations (Figure 5.25). The concentrations were found to be highest near the source in MP-3-4 and generally decreased along the flow path. The concentrations of 1,1-DCE, ranging from 0 to 3,100 μg/L (Figure 5.26), were relatively low compared to the cis-DCE concentrations. The pattern of 1,1-DCE concentrations was similar to cis-DCE.

The concentrations of both VC and ethene in Layer 5 were generally below 1,000 μg/L, indicating a minor degradation of the DCEs (Appendix IV). The highest concentrations were found near the source in wells MP-3-4 (920 μg/L and 1,395 μg/L, respectively) and P-115 (1,200 μg/L and 436 μg/L, respectively), which was the most reducing area.

cis-DCE was the dominant compound (more than 80%) in the area from the source to the middle of the plume in the wells MP-3-4, P-115, P-164, P-71, P-145, P-153, P-156, P-132 and P-160 (Figure 5.27). The minor components were 1,1-DCE, VC, and ethene, which were less than 20% in total. Based on the low percentages of PCE and TCE and high percentages of cis-DCE, it was concluded that complete transformation from PCE and TCE to at least cis-DCE had been achieved in this area. The low concentrations of VC and ethene could be caused either by insignificant biodegradation

of cis-DCE or fast consumption of these two compounds. Stable carbon isotopes will be used to further examine the degree of the degradation of cis-DCE in the next section.

The composition at the edge of the plume in wells P-131, P-136, P-140, MP-8-10, and P-129, was approximately 50% TCE, 25% cis-DCE, and 25% of 1,1-DCE and PCE. This composition was quite different from the composition in the middle of the plume, and it was similarly to the pattern observed from the previous years, in the Historical Data Review in Section 5.1.2. It was noted that the well P-116, which was near the extraction well P-145 near the middle of the plume, had an composition (about 50% of cis-DCE and 30% of TCE) closer to the composition at the edge of the plume than in the middle of the plume (Figure 5.27). This pattern was probably caused by the extraction in the well P-145 of the Hydraulic Barrier System, which brought groundwater at the edge of the plume to the middle.

This pattern of cis-DCE dominant in the middle of the plume and TCE dominant at the edge of the plume in Layer 5 was likely caused by the two phases of degradation at the site. The TCE dominant composition at the edge of the plume corresponded to the first phase (see Historical Data Review), when significant degradation of chlorinated compounds had not occur in the downgradient area and the precursors were transported through the aquifer with minor degradation. The cis-DCE dominant composition in the area from the source to the middle of the plume corresponded to the second phase, when significant degradation of PCE and TCE to cis-DCE occurred in the downgradient area. The emergence of cis-DCE at the edge of the plume in 2007 (Figure 5.27) reflected the more recent composition in the upgradient wells, since the redox conditions at the edge of the plume were not at all suitable for biodegradation of TCE to cis-DCE. The second phase was likely caused by the introduction of large amounts of BTEX and ketones by

the DNAPL pumping in the source zone, as stated in the Historical Data review in section 5.1.2.

Chlorinated Ethanes The concentrations of 1,1,1-TCA in Layer 5 ranged from 0 to 6,900 µ g/L, with the highest concentration observed near the source zone in MP-3-4 (Appendix IV). Concentrations were also higher in the center of the plume in wells P-153 and P-156 (4,000 µ g/L and 2,200 µ g/L respectively). The concentrations of 1,1-DCA was highest near the source zone in well MP-3-4 (59,000 µ g/L) and decreased rapidly to the downgradient (Appendix IV). Concentrations of chloroethane were significant only in three wells, MP-3-4 (3,100 µ g/L) near the source, P-116 (3,000 µ g/L) in the middle of the plume, and P-136 (1,400 µ g/L) at the edge of the plume (Appendix IV). By contrast, most of the other wells had nondetectable chloroethane concentrations, making the pattern of chloroethane concentration difficult to interpret. Ethane, a potential degradation product of chloroethane was only found near the source in MP-3-4, with a small concentration of 33 µ g/L.

Degradation of 1,1,1-TCA to 1,1-DCA was observed to be incomplete from the source to the middle of the plume (Figure 5.28), in contrast to complete degradation of TCE to cis-DCE (Figure 5.27). The composition gradually changed from 1,1-DCA dominant near the source zone to 1,1,1-TCA dominant at the edge of the plume. The pattern was especially clear in the area outlined by the dashed black line (Figure 5.28). The percentage of 1,1,1-TCA changed from less than 10 percent near the source in MP-3-4, to more than 10 percent further to the east in P-115 and P-164, to about half near the middle of the plume in P-145, to more than 60 percent in the center of the plume in P-156 and P-153, and finally to more than 95 percent near the front of the plume in P-160, P-132 and P-129. The pattern of distribution of chlorinated ethanes is different from the pattern of distribution of chlorinated ethenes, as clear decreasing degradation extent can

be seen from the source to the middle of the plume compared to solely cis-DCE in the same area. This difference is likely caused by much faster degradation of TCE than 1,1,1-TCA. This is also observed in the Historical Data Review in Section 5.1.2 and 5.1.3.

In the other layers, well P-53 in Layer 2 near the source zone had 32,000 µ g/L of cis-DCE, 1,000 µ g/L of 1,1-DCE, 16000 µ g/L of VC, 19000 µ g/L of 1,1-DCA, and 15646 µ g/L of ethene and almost undetectable concentrations of PCE, TCE, 1,1,1-TCA and chloroethane. The composition and concentration of chlorinated compounds in well P-53 indicated significant amounts of degradation of chlorinated ethenes to ethene and complete transformation from 1,1,1-TCA to 1,1-DCA. The very large extent of degradation in this well is consistent with the very reducing (methanogenic) conditions in the area of well P-53. Well MP-3-1 in Layer 3 had a relatively low total chlorinated compounds concentration (about 2,300 µ g/L), but the compounds were almost entirely composed of 1,1-DCA (330 µ g/L) and ethene (1960 µ g/L), indicating large extent of degradation, which was also consistent with the methanogenic conditions in this well. Wells P-53 and MP-3-1 also had relatively high ketones and BTEX concentrations (compared to their total chlorinated compounds concentrations). The other selected sampling wells located in layers besides Layer 5 generally had quite low concentrations of chlorinated compounds and not too much degradation as expected.

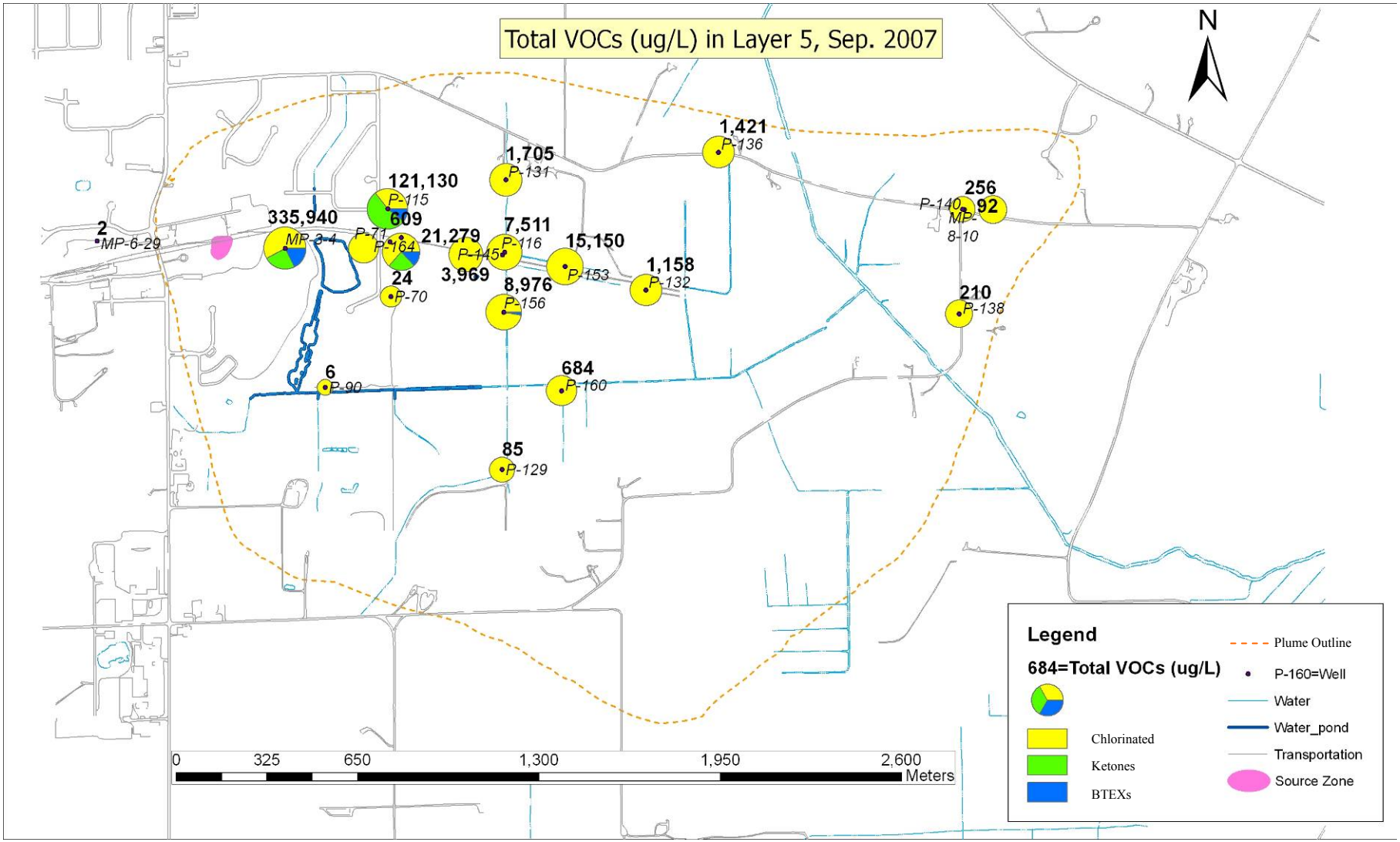


Figure 5.24 Composition of VOCs in Layer 5 in September 2007

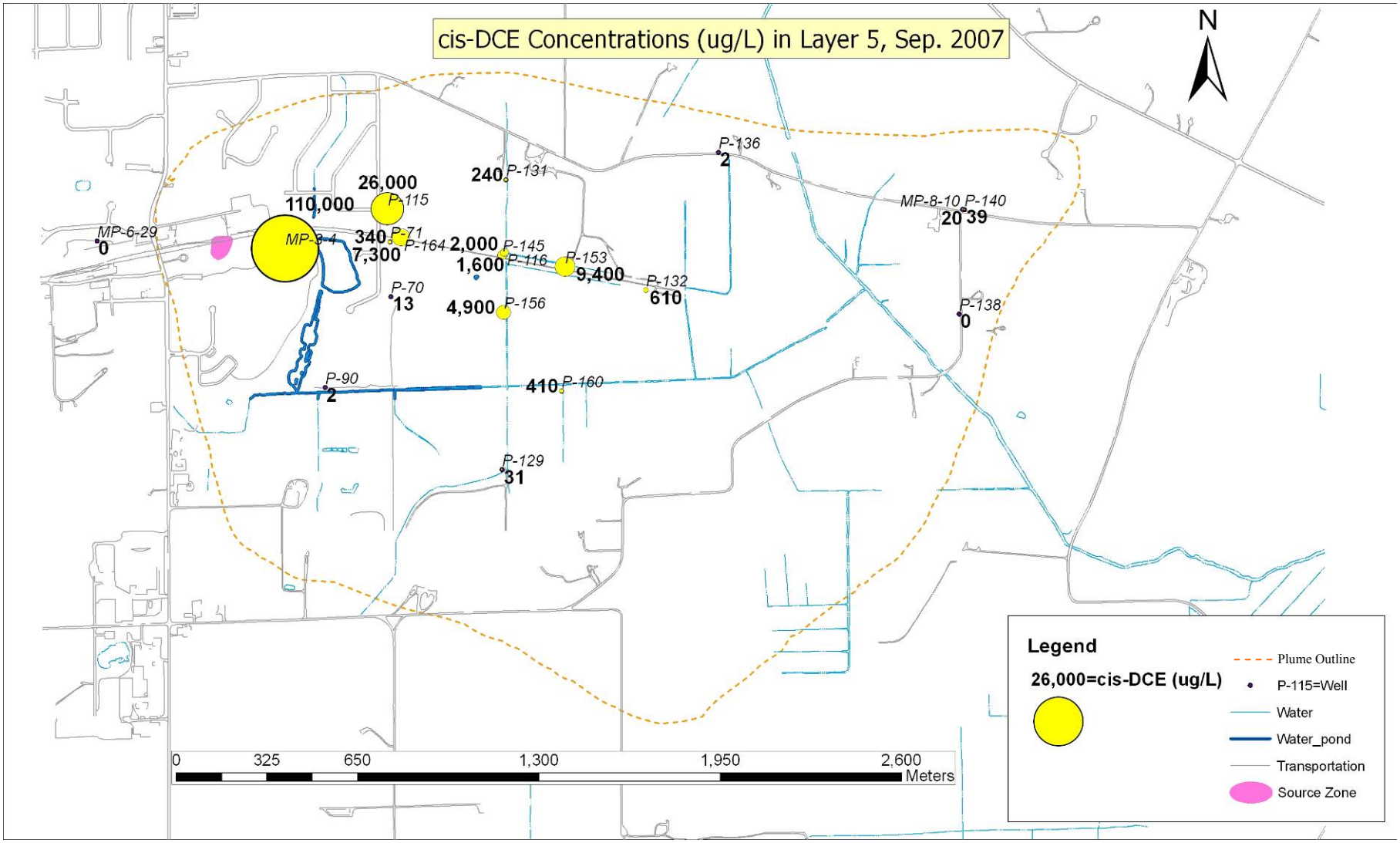


Figure 5.25 Concentration of cis-DCE (μ g/L) in Layer 5 in September 2007

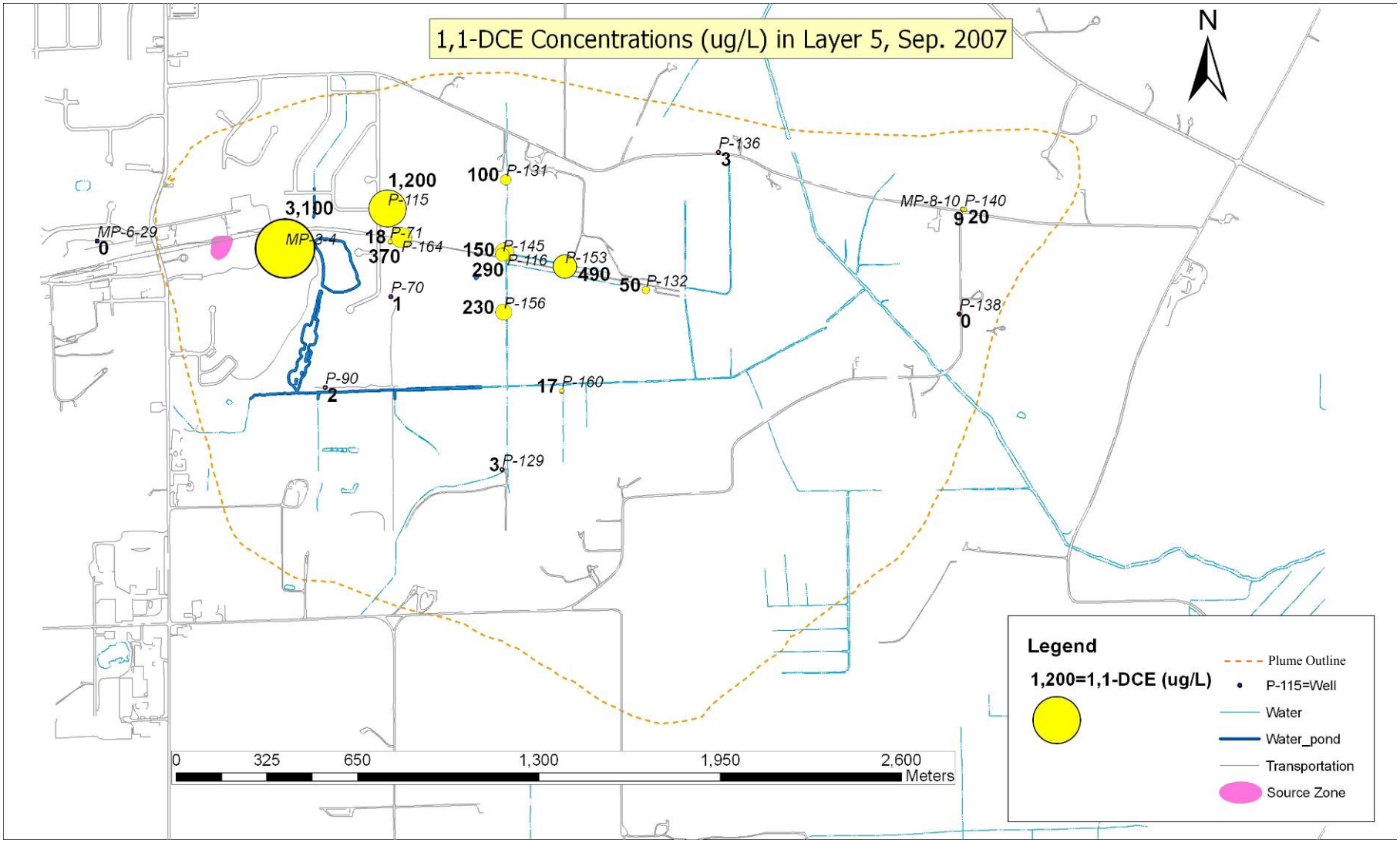


Figure 5.26 Concentration of 1,1-DCE (μ g/L) in Layer 5 in September 2007

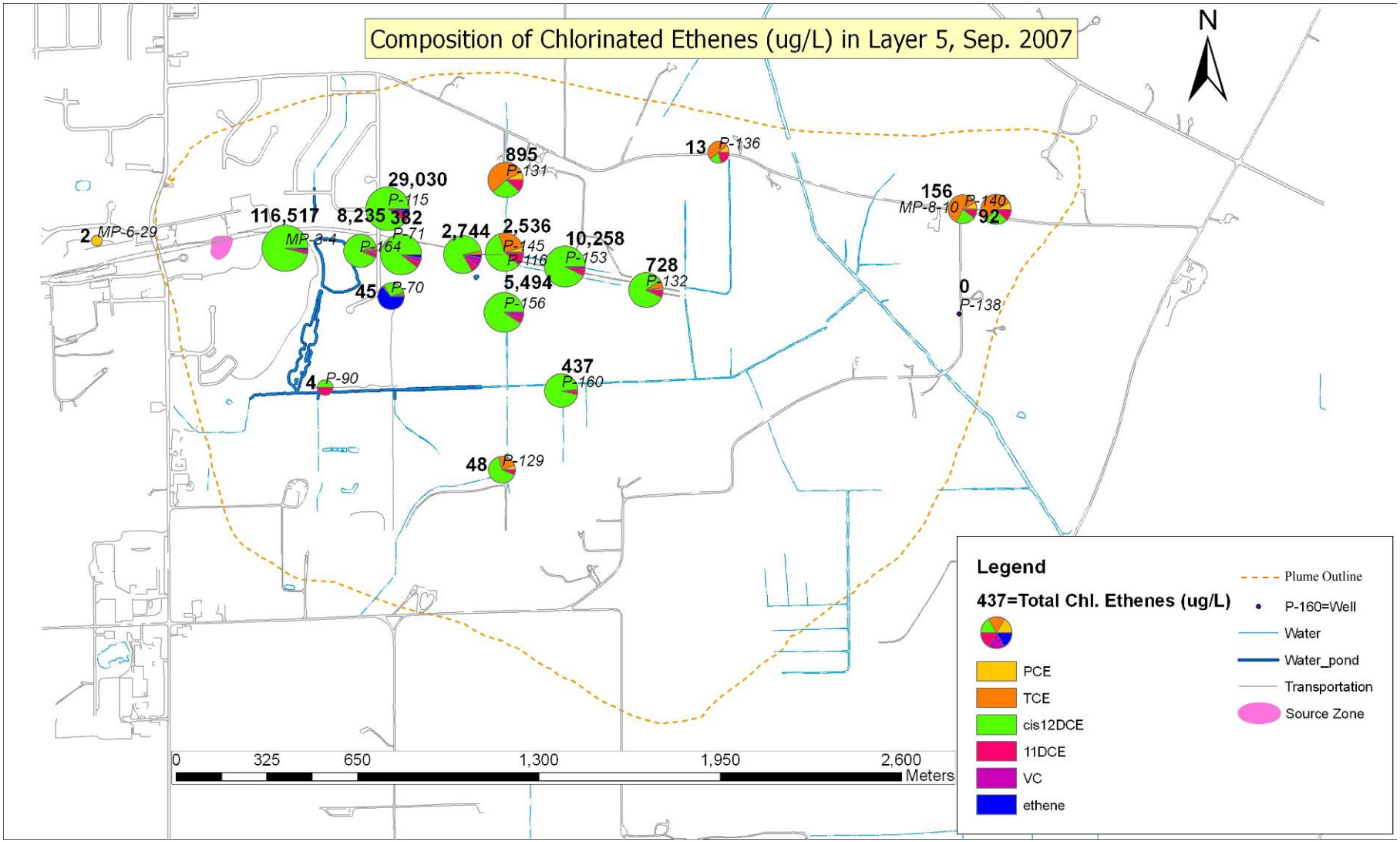


Figure 5.27 Composition of Chlorinated Ethenes in Layer 5 in September 2007

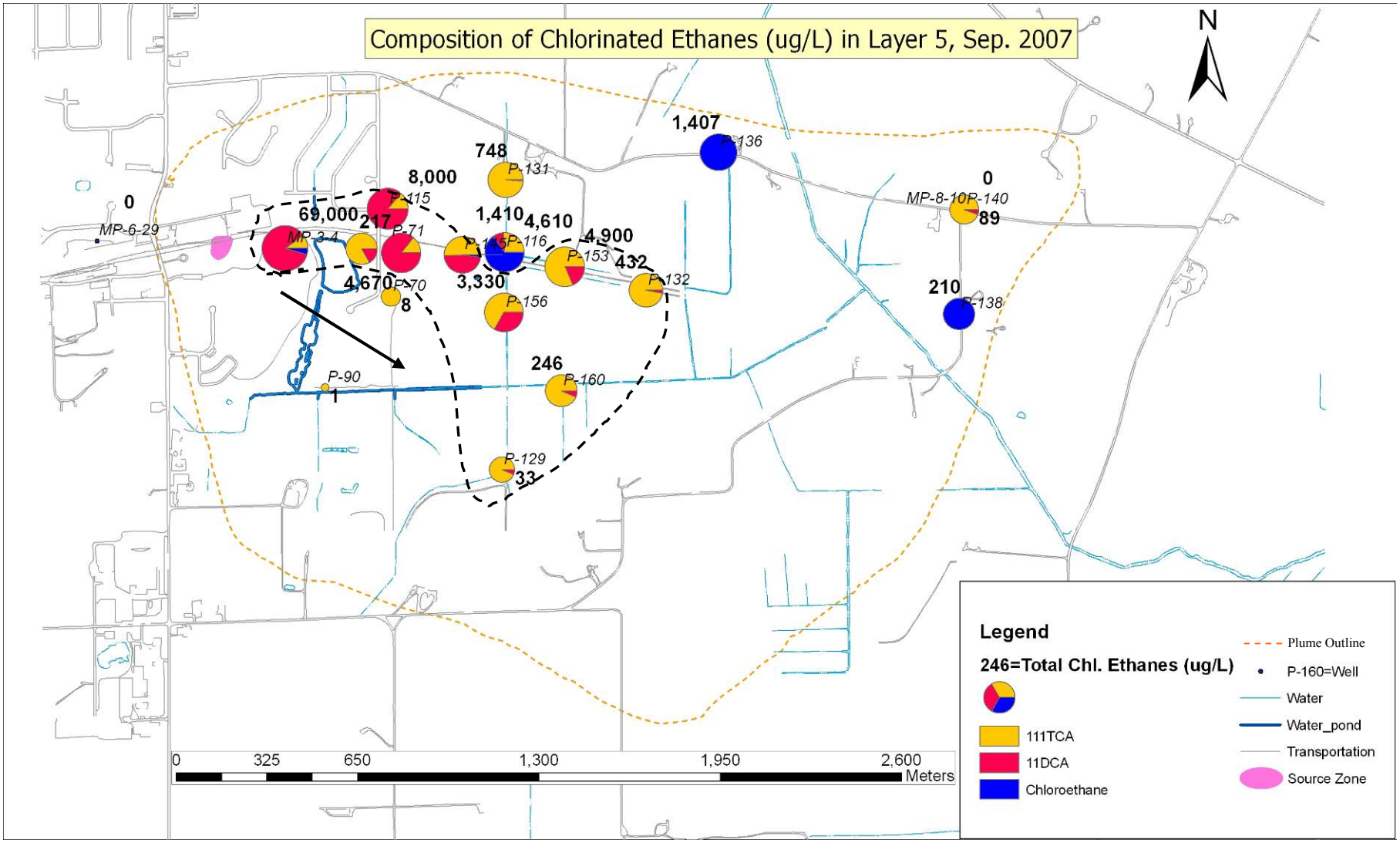


Figure 5.28 Composition of Chlorinated Ethanes in Layer 5 in September 2007

5.2.4 Carbon Isotopes of Major Chlorinated Compounds

Chlorinated Ethenes The $\delta^{13}C$ values of PCE in Layer 5 ranged from -29.2‰ to -17.2‰ (Appendix V). The most enriched value was found in the center of the plume in P-153 and the most depleted value was found at the edge of the plume in P-131 (Figure 5.29). The $\delta^{13}C$ values of TCE in Layer 5 ranged from -28.5‰ to -14.7‰ (Appendix V). The most enriched value was found in the center of the plume in P-153 and more depleted values were found in the areas at the edge of the plume and near the source (Figure 5.30). The most reducing area of the plume, determined to be near the source, did not correspond to the most enriched $\delta^{13}C$ values of PCE or TCE. However, the aerobic area at the edge of the plume corresponded to the most depleted $\delta^{13}C$ values of PCE or TCE.

The $\delta^{13}C$ values of cis-DCE in Layer 5 were in a range of -28.4‰ to -23.5‰, with the most enriched value found near the middle of the plume in P-145 and the most depleted values found at the edge of the plume and near the source (Figure 5.31) (Appendix V). Again, the most reducing area near the source did not correspond to the most enriched $\delta^{13}C$ values (in contrary, corresponded to some depleted values) while the aerobic area at the edge of the plume corresponded to the most depleted values. The area near the source in Layer 2 had a $\delta^{13}C$ value of -15.06‰ for cis-DCE in well P-53, which was much more enriched than the values in Layer 5. This indicates much greater degree of degradation of cis-DCE in Layer 2 than in Layer 5, consistent with the high concentrations of VC and ethene (16,000 and 15,646 μg/L, respectively) and the more reducing conditions (methanogenic) in this area in Layer 2 than in Layer 5.

The extent of degradation of chlorinated ethenes in Layer 5 was determined from the carbon isotopes of cis-DCE. It was observed that the $\delta^{13}C$ values of cis-DCE in Layer 5 (Figure 5.31) were only slightly enriched than the original $\delta^{13}C$ value of PCE or TCE,

which can be determined to be about -30‰ from the most negative $\delta^{13}C$ values for PCE and TCE. This slight enrichment confirmed that there was no significant degradation of cis-DCE, which was in agreement with the low concentrations of VC and ethene. Based on the pattern described in the Introduction (Figure 1.3), when there is no degradation of cis-DCE its $\delta^{13}C$ value finally evolves to the original $\delta^{13}C$ value of the precursors, PCE or TCE. Therefore, combining the composition of chlorinated ethenes stated in the previous section and the carbon isotopes of cis-DCE, it can be concluded that complete transformation from PCE and TCE to cis-DCE was achieved in the middle of the plume, with little degradation of cis-DCE. Degradation might have the potential to proceed to VC and ethene in the future because small amounts of VC and ethene had emerged recently.

The $\delta^{13}C$ values of 1,1-DCE in Layer 5 ranged from -28.7‰ to -18.6‰, with the most enriched value found in the middle of the plume and the most depleted value near the source (Figure 5.32) (Appendix V). The most depleted value near the source likely represented the original $\delta^{13}C$ value of the 1,1-DCE newly dissolved from the DNAPL, which was -28.7‰, similar to the original $\delta^{13}C$ value of the cis-DCE (-28.4‰). The enrichment factor for biodegradation of cis-DCE ranged from -14.1‰ to -20.4‰ (Bloom et al., 2000 ; Slater et al., 2001 ; Hunkeler et al., 2002), while the enrichment factor for biodegradation of 1,1-DCE was reported to be -7.3‰ (Hunkeler et al., 2002). A compound with a less negative enrichment factor gains less enrichment when it undergoes certain amount (fraction) of degradation. In general, the $\delta^{13}C$ values of 1,1-DCE, with most of the values in the range of -25‰ to -20‰, were more enriched than the $\delta^{13}C$ values of cis-DCE, with most of the values in the range of -28‰ to -26‰. Thus, the degradation of 1,1-DCE should be much more significant than cis-DCE, given the similar original $\delta^{13}C$ values, the less negative enrichment factor, and the more

enriched $\delta^{13}C$ values. The area near the source in Layer 2 also had a much more enriched $\delta^{13}C$ value of 1,1-DCE (-10.33‰) in well P-53, consistent with the greater degree of degradation in Layer 2.

It was observed that although the concentration fractions of PCE and TCE changed considerably along the flow path, most of the $\delta^{13}C$ values of PCE and TCE were around -25‰ (Figure 5.33). Residual PCE and TCE concentration fractions were only about one and five percent, respectively, in the wells P-71, P-145, and P-132. Usually, such low concentration fractions should result in much more enriched $\delta^{13}C$ values than those observed in these wells (-25‰).

The expected $\delta^{13}C$ values of PCE and TCE in wells P-71, P-145, and P-132 with the observed concentration fractions of PCE and TCE can be calculated by the equation

$$\ln\left(\frac{\delta^{13}C+1}{\delta^{13}C_0+1}\right) = \varepsilon \ln f$$

where $\delta^{13}C$ is the $\delta^{13}C$ value of the residual PCE or TCE, $\delta^{13}C_0$ is the initial $\delta^{13}C$ value, f is the residual concentration fraction, and ε is the enrichment factor. If the enrichment factor for reductive dechlorination of PCE is assumed conservatively to be -3‰ based on reported values (ε=-2‰ in a microcosm experiment by Hunkeler et al., 1999; ε=-5.5‰ in a study using a microbial consortium and butyric acid by Slater et al., 2001), the initial $\delta^{13}C$ value of PCE is -30‰, and f is estimated to be 1/30 based on the percent of PCE in wells P-71, P-145 and P-132 (1 percent) and in non-degraded groundwater (30 percent), we would have

$$\ln\left(\frac{\delta^{13}C+1}{-0.030+1}\right) = -0.003\ln\left(\frac{1}{30}\right)$$

$$\rightarrow \delta^{13}C=-0.020=-20\text{ ‰ for PCE.}$$

For TCE, the enrichment factor is assumed conservatively to be -5‰, based on reported values of -2.5‰ to -13.8‰ (Hunkeler et al., 1999; Bloom et al., 2000; Slater et al., 2001). The initial $\delta^{13}C$ value of PCE is also -30‰. Because the degradation of PCE to TCE was almost complete and PCE and TCE had similar original $\delta^{13}C$ values, the original composition before degradation (30% of PCE and 70% of TCE) can be treated as 100% of TCE. Therefore, f is estimated to be 0.05, which is the percentage of TCE after degradation in wells P-71, P-145 and P-132. We would have

$$\ln\left(\frac{\delta^{13}C+1}{-0.030+1}\right) = -0.005\ln(0.05)$$

$$\rightarrow \delta^{13}C=-0.0154=-15.4\text{‰ for TCE.}$$

The expected $\delta^{13}C$ values of the residual PCE and TCE are calculated to be -20‰ and -15.4‰ respectively, which are much more enriched than the observed $\delta^{13}C$ values (about -25‰) in wells P-71, P-145 and P-132 (Figure 5.33). The lower enrichment observed in these wells might be caused by back diffusion of less-degraded PCE and TCE stored in the matrix into the fractures, when the groundwater containing small amounts of highly-degraded PCE and TCE reached these fractures. The PCE and TCE stored in the matrix in the early years before significant degradation occurred should have $\delta^{13}C$ values close to the original $\delta^{13}C$ values (-30‰). The residual PCE and TCE in the groundwater in the fractures transported from the upgradient after significant degradation occurred should have enriched $\delta^{13}C$ values, close to those calculated ones above (more enriched than -20‰). The residual PCE and TCE were blended with the PCE and TCE released from the matrix, resulting in the observed $\delta^{13}C$ values (around -25‰)

Chlorinated Ethanes The $\delta^{13}C$ values of 1,1,1-TCA ranged from -26.3‰ to -23.5‰ (Appendix V) and showed a trend of less enriched values towards the edge of the plume. The values changed from -23.5‰ near the source in MP-3-4, to around -25.5‰ near the

front of the plume in P-129, P-160, and P-132 (Figure 5.34). This pattern was consistent with the composition distribution of chlorinated ethanes, which exhibited a decreasing degree of degradation of 1,1,1-TCA from the source zone to the edge of the plume (Figure 5.34).

1,1-DCA derived from biodegradation of 1,1,1-TCA, thus the $\delta^{13}C$ values of 1,1-DCA were more depleted than 1,1,1-TCA, ranging from -33.4‰ to -24.4‰ (Figure 5.35) (Appendix V). The values changed from -25.6‰ near the source in well MP-3-4 to -33.4‰ near the front of the plume in P-160 (Figure 5.35), similarly to the pattern of 1,1,1-TCA. The pattern also corresponded well with the composition distribution of chlorinated ethanes. It was noted that the original $\delta^{13}C$ value of 1,1,1-TCA was about -26‰ determined from well P-132, where the composition was almost entirely 1,1,1-TCA and the initial $\delta^{13}C$ value of 1,1-DCA was about -33.4‰ determined from well P-160, where the production of 1,1-DCA just started. The enrichment factor for biodegradation of 1,1,1-TCA to 1,1-DCA can be estimated to be -33.4‰ - (-26‰) = -7.4‰. The area near the source in Layer 2 again had a much more enriched $\delta^{13}C$ value of 1,1-DCA (-19.01‰) in well P-53, consistent with the greater degree of degradation in Layer 2. Well MP-3-1 in Layer 3, had a very enriched $\delta^{13}C$ value of 1,1-DCA (-6.85‰) compared to the other $\delta^{13}C$ values of 1,1-DCA. It had 1,1,1-TCA, 1,1-DCA, and chloroethane concentrations of 0, 330 μ g/L, and 4 μ g/L, respectively. The enriched $\delta^{13}C$ value of 1,1-DCA indicated significant degradation of 1,1-DCA to chloroethane. But the chloroethane concentration was very low, probably due to fast degradation of chloroethane.

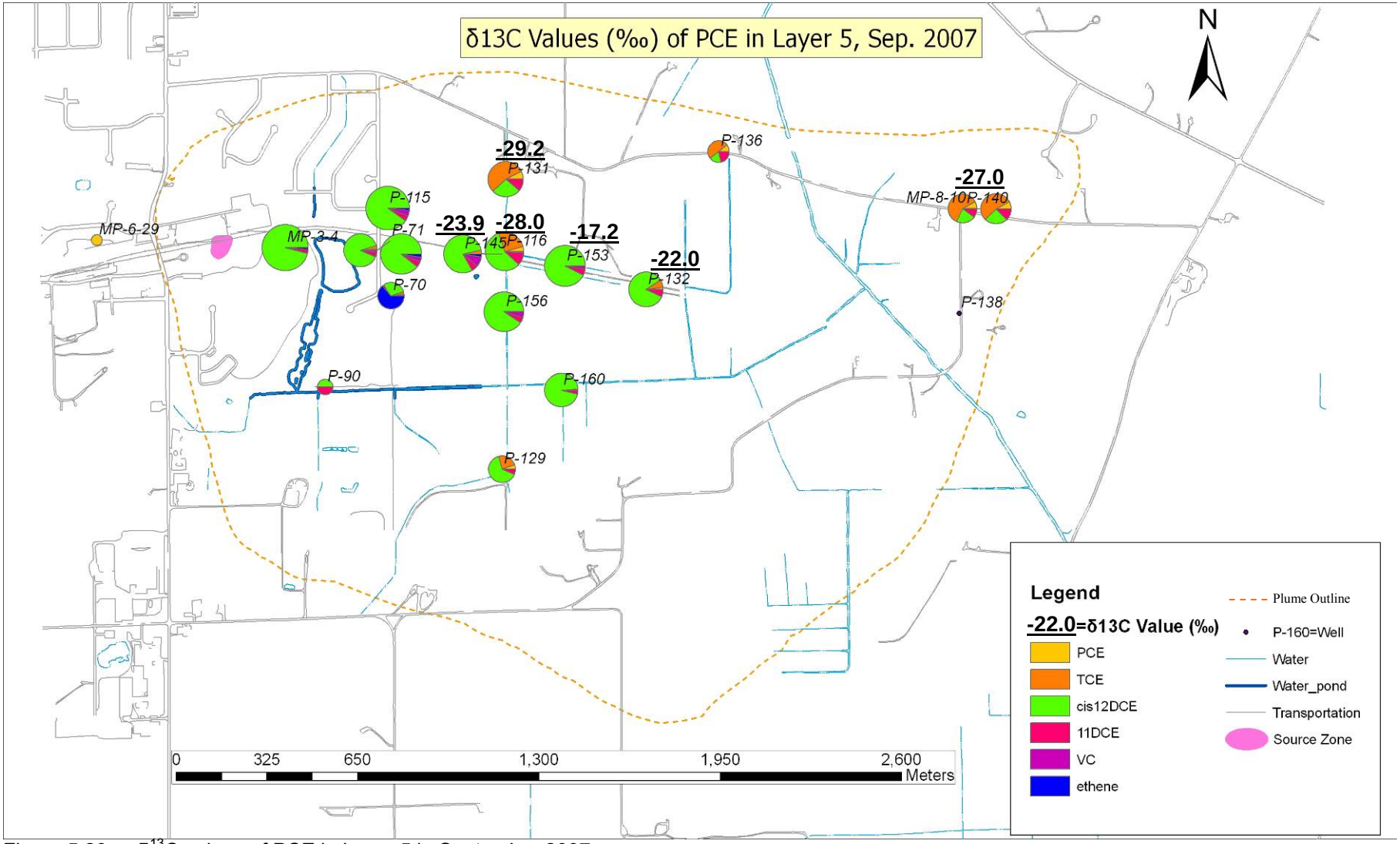


Figure 5.29 $\delta^{13}C$ values of PCE in Layer 5 in September 2007

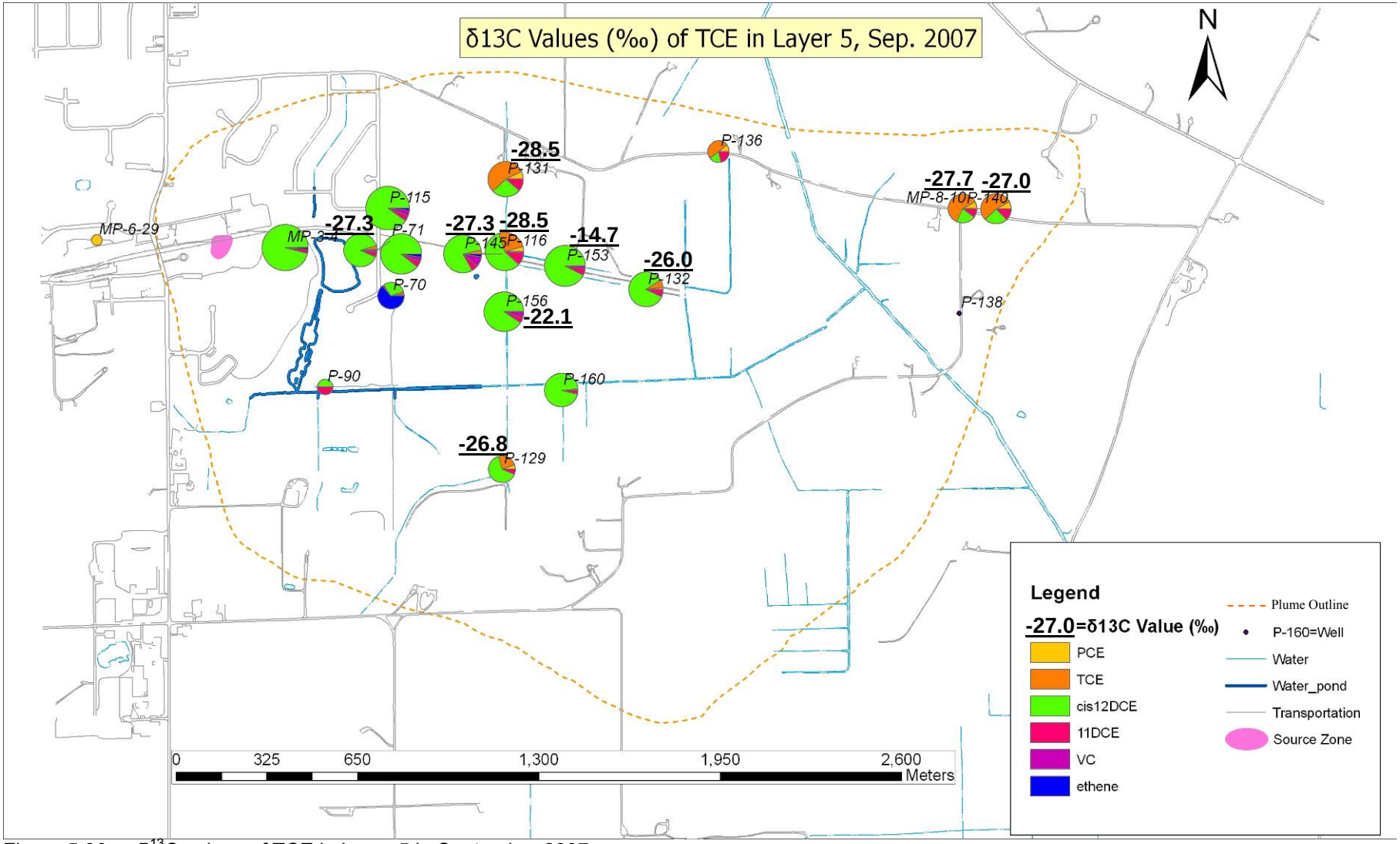


Figure 5.30 $\delta^{13}C$ values of TCE in Layer 5 in September 2007

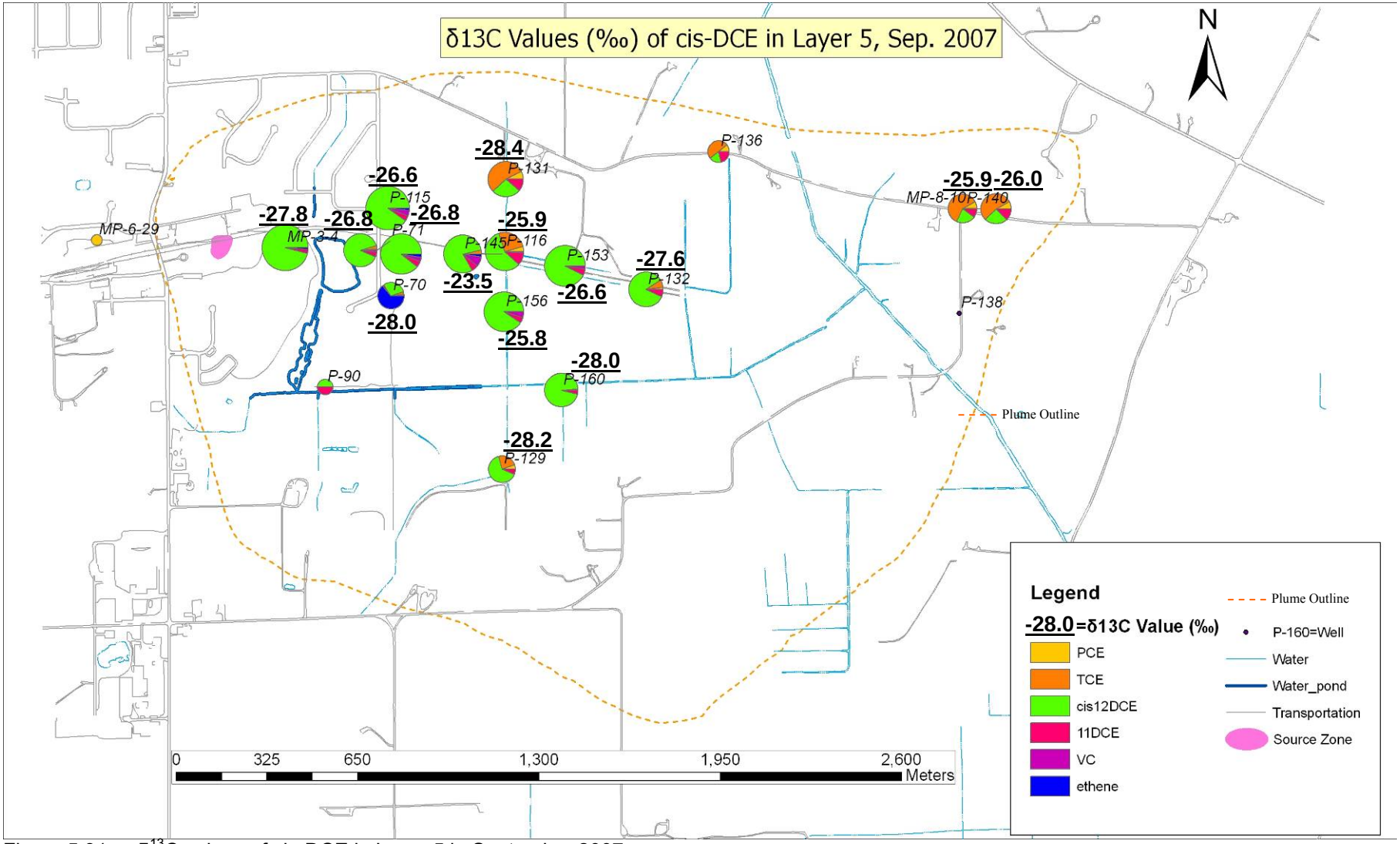


Figure 5.31 $\delta^{13}C$ values of cis-DCE in Layer 5 in September 2007

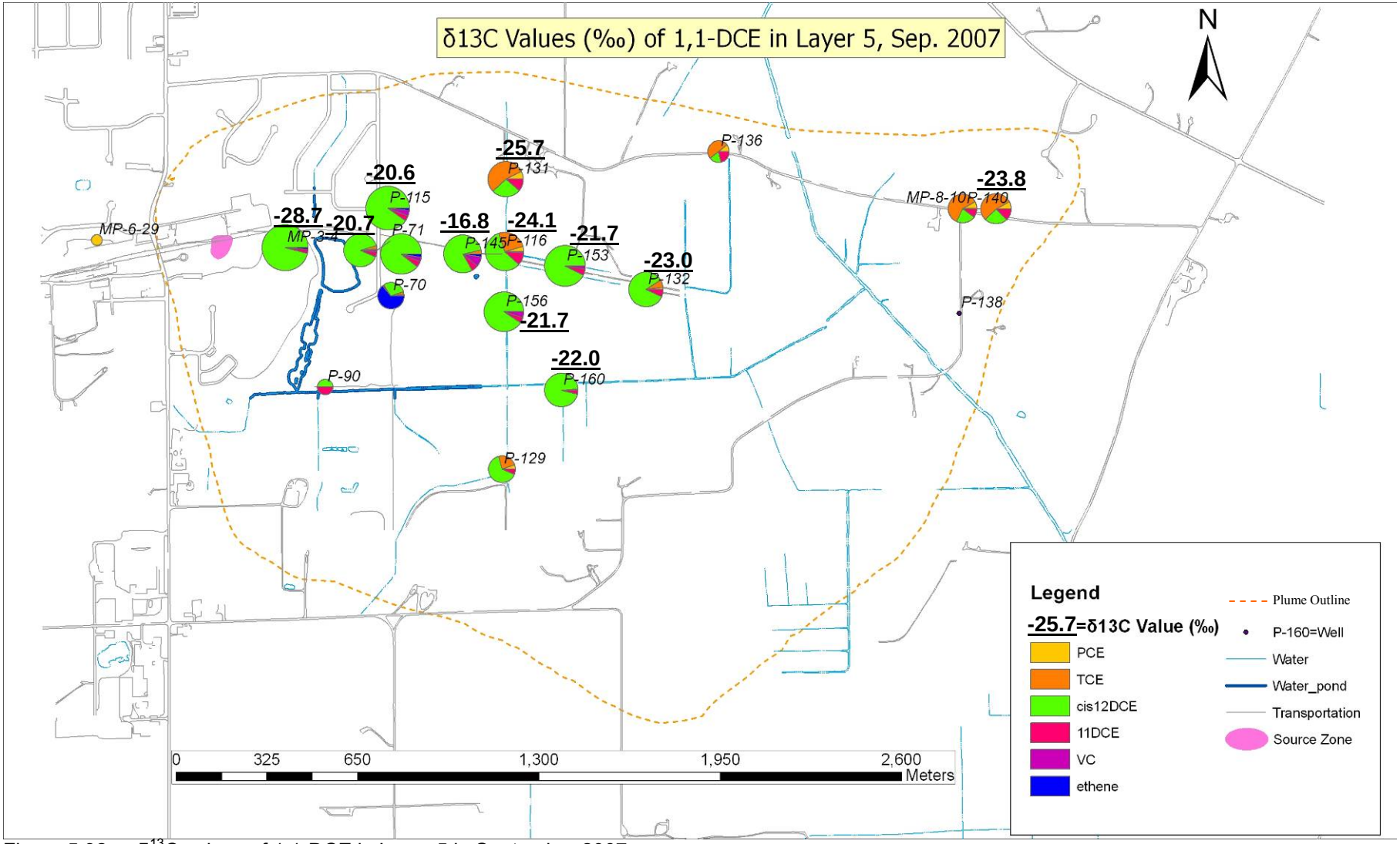


Figure 5.32 $\delta^{13}C$ values of 1,1-DCE in Layer 5 in September 2007

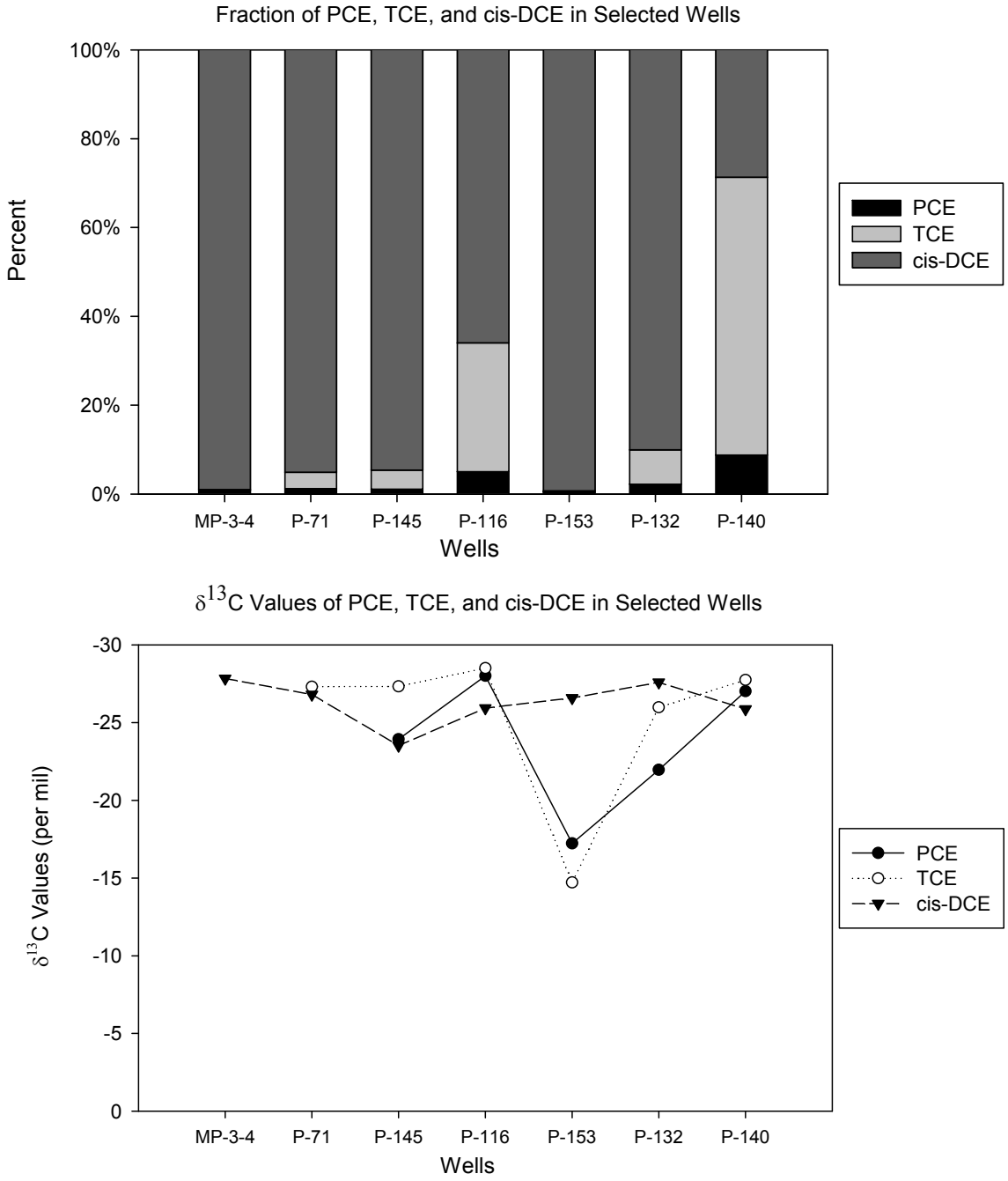


Figure 5.33 Fraction and δ^{13}C values of PCE, TCE, and cis-DCE in Selected Wells in Layer 5 in September 2007

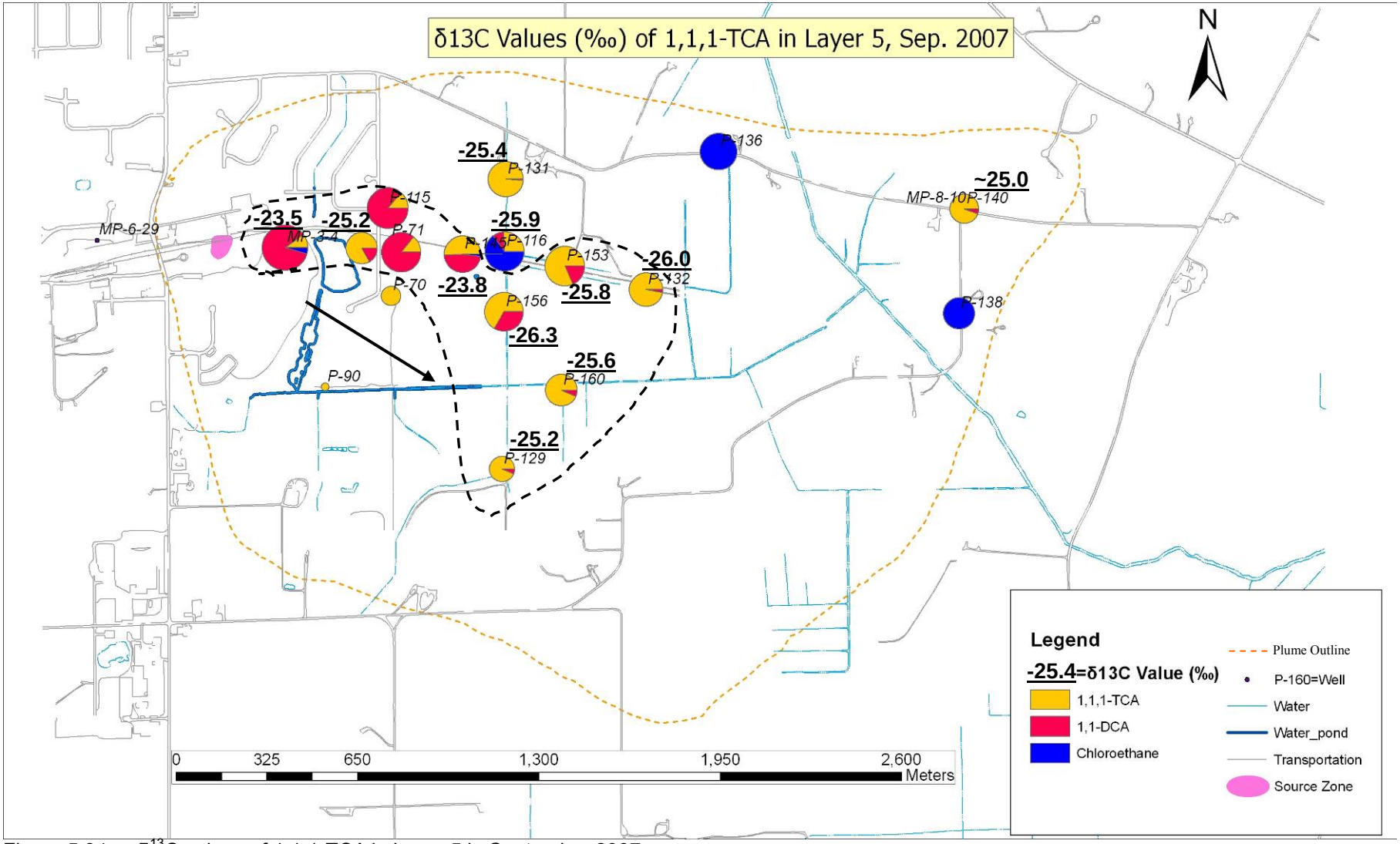


Figure 5.34 $\delta^{13}C$ values of 1,1,1-TCA in Layer 5 in September 2007

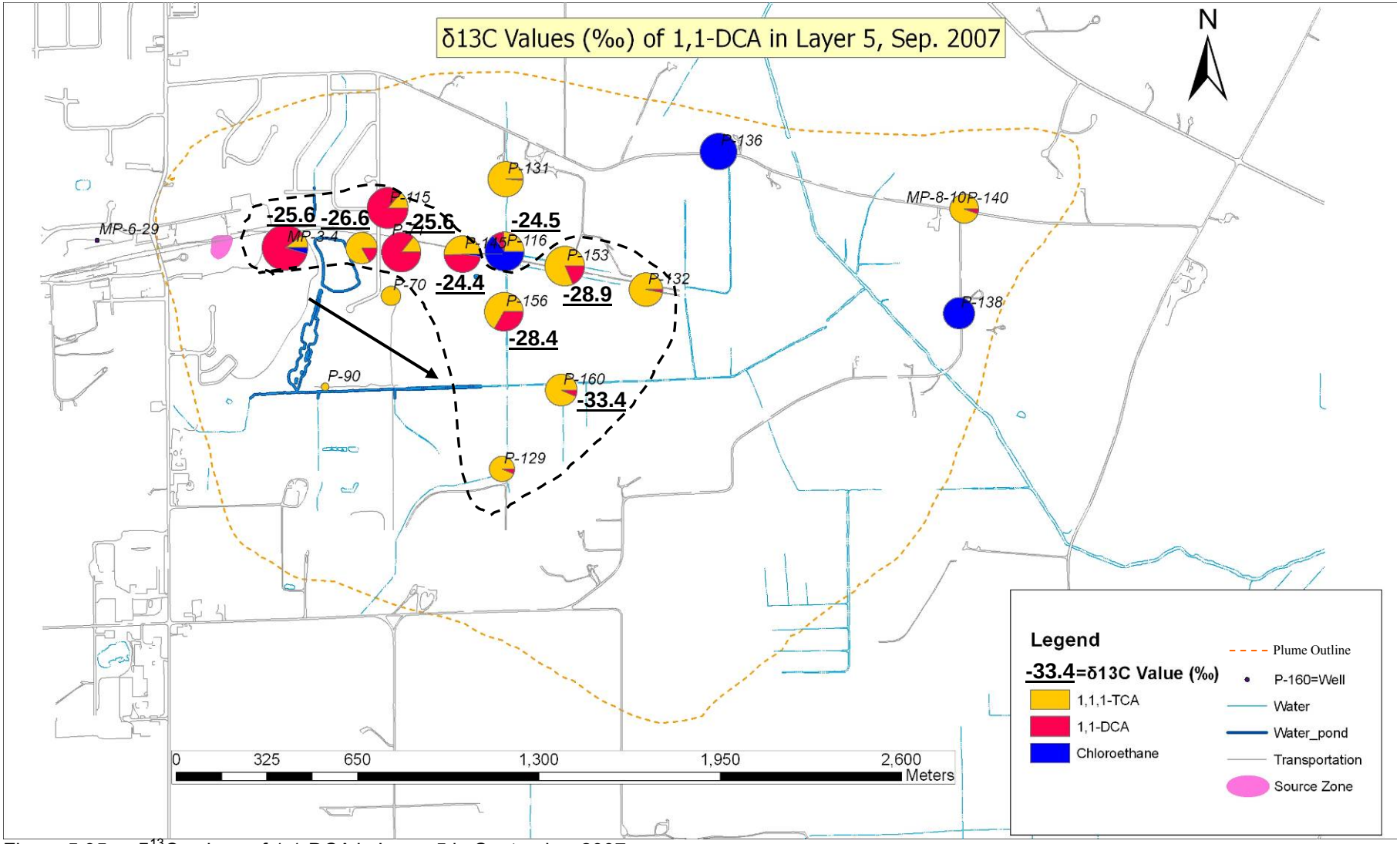


Figure 5.35 $\delta^{13}C$ values of 1,1-DCA in Layer 5 in September 2007

6 Summary and Conclusions

This study have shown that a combined analysis of long term VOC concentration data with VOC, geochemical and carbon isotope data collected in the present study has provided a comprehensive understanding of the composition of the VOC plume in the fracture rock aquifer. The data interpretation focused on the present degradation patterns and the history of the contaminant plume.

6.1 VOC Degradation Extent

The composition of chlorinated ethenes in Layer 5 indicates that PCE and TCE were nearly completely degraded to cis-DCE in the area from the source to the middle of the plume in contrast to about 40% of biodegradation of PCE and TCE to cis-DCE was observed at the fringe of the plume. However, the degree of degradation of cis-DCE could not be confidently determined only based on the VOC composition. The $\delta^{13}C$ values of cis-DCE were very similar than the original $\delta^{13}C$ values of PCE and TCE confirming that degradation of the cis-DCE to VC was minor in Layer 5. However, further degradation beyond cis-DCE might occur in a near future depending on the availability of sufficient electron donors to maintain the redox conditions as well as specialized microorganisms for degradation of cis-DCE to VC and ethene. This pattern is observed in Layer 2 where the concentration and carbon isotope data showed that biodegradation of PCE and TCE continue after cis-DCE with the formation of VC.

The extent of the degradation of chlorinated ethenes was consistent with the redox condition, which seems to be controlled by the amounts of BTEX and ketones concentration in Layer 5 (September 2007) discussed in section 5.2.3. The anaerobic conditions in the area from the source to the middle of the plume corresponded to the cis-DCE dominated zone and the aerobic conditions at the edge of the plume

corresponded to the TCE dominated zone. Within the anaerobic zone, redox conditions generally became less reducing further away from the source zone, corresponding to a decreasing potential for degradation of chlorinated ethenes. Biodegradation of TCE to DCEs requires at least iron reducing conditions (Bradley, 2000). However, only the part of the aquifer near the source was determined to be under at least iron reducing conditions while further downgradient, manganese reducing or aerobic conditions prevailed. Consequently, it seemed that the cis-DCE dominated composition in the middle of the plume originated from biodegradation of PCE and TCE from the upgradient area near the DNALP source.

The aerobic redox condition at the edge of the plume was not at all suitable for biodegradation of TCE to cis-DCE, though cis-DCE did start to be detected during the recently. Again this was probably caused by formation and transport of cis-DCE from the upgradient part of the aquifer. Much more reducing conditions and higher concentration of electron donors were observed in Layer 2, which explained the further degradation of cis-DCE to VC in Layer 2.

The composition of chlorinated ethanes showed that the degradation extent of 1,1,1-TCA generally decreased from about 80% near the DNALP source to less than 4% at the edge of the plume. The $\delta^{13}C$ values of 1,1,1-TCA and 1,1-DCA confirmed the pattern of decreasing degradation of 1,1,1-TCA to 1,1-DCA from the source to the edge of the plume. The pattern was consistent with the less reducing redox conditions further away from the source. Appreciable amounts of chloroethane were only seen in few of the wells, indicating little degradation from 1,1-DCA to chloroethane. It seems that based on the less extent of degradation of 1,1,1-TCA than TCE even more reducing conditions are required for the biodegradation of chlorinated ethanes than that of chlorinated ethenes.

The redox condition (controlled by the distribution of BTEX and ketones) can be linked to the history of the site, which showed that the degradation of TCE to cis-DCE and 1,1,1-TCA to 1,1-DCA was triggered by the release of large amounts of BTEX and ketones into Layer 5 caused by the large scale DNAPL pumping in the source starting in 1999. Historical data also showed that both chlorinated ethenes and ethanes were observed to degrade faster (or earlier) in Layer 2 than in Layer 5, likely caused by earlier presence of large amounts of BTEX and ketones in Layer 2 than in Layer 5, again highlighting the importance of the presence of electron donors to create suitable redox conditions and serve as substrates for the degradation of chlorinated compounds. In both layers, it was observed that the degradation of TCE were faster than that of 1,1,1-TCA, indicating that chlorinated ethanes might be more persistent than chlorinated ethenes.

6.2 Degradation History

The historical data from 1992 to 2006 showed three stages of degradation in Layer 5. The first stage corresponded with the period before June 1998, before DNAPL pumping when a short VOC plume developed in the main groundwater flow direction. This stage was characterized by relative low chlorinated compounds concentrations in the layer (below 100,000 µ g/L in the most contaminated well MP-3-4), almost no ketones and BTEX, and no clear evidence of biodegradation of PCE/TEC and 1,1,1 TCA to cis-DCE and 1,1-DCA, respectively. The second stage corresponded with the period between September 1998 and June 1999, which was after a pilot DNAPL pumping test in a recovery well RW-58. This stage was characterized by an increase in chlorinated compounds concentration up to about 400,000 µ g/L in the most contaminated well MP-3-4, a short plume in the main groundwater flow direction, relatively low BTEX and almost no ketones , and almost no biodegradation of PCE/TEC and 1,1,1 TCA to cis-DCE and 1,1-DCA, respectively. The third stage corresponded to the period from September 1999 to the present, which was after the start of large scale DNAPL pumping test during the months of August through the first week of November 1999. This stage was characterized by relative high concentrations of chlorinated compounds (300,000 µ g/L in well MP-3-4), a much longer plume in the main flow direction, high concentration of ketones (up to about 900,000 µ g/L) and BTEX (about 100,000 µ g/L) in the most contaminated well MP-3-4, and significant VOC biodegradation to cis-DCE and 1,1-DCA in the area near the source zone and in the middle of the plume. At the end of the third stage (from about 2005), VOC concentration started to decline, which was thought to be caused by the operation of the Hydraulic Barrier System in the middle of the plume which started to operate since October 2003.

Summarizing, the long term pattern of VOC, Ketones and BTEX concentration and the degree of VOC biodegradation seems to be controlled by the DNAPL pumping (the pilot one in 1998 and the subsequent large scale ones after August 1999). It is hypothesized that the DNAPL pumping might have opened groundwater flow channels in the bulk DNAPL body and enhanced dissolution causing a huge increase of contaminant concentrations in the downgradient areas (the area near the source where well MP-3-4 was located and the areas further to the east). Especially, the large scale DNAPL pumping in 1999 mobilized large amounts of BTEX and ketones into Layer 5 creating reducing redox conditions in the aquifer and they also served as electron donors inducing the significant degradation of PCE/TCE to cis-DCE and 1,1,1-TCA to 1,1-DCA.

The degradation history of the site was also partly influenced by the creation of a Hydraulic Barrier System in the middle of the plume, which consists of four extraction wells operated from October 2003. This Hydraulic Barrier System has significantly lowered the contaminant concentrations in the downgradient area, especially in the area between the two extraction wells P-164 and P-145. The redox conditions in the aquifer have also been modified by the operation of the Hydraulic Barrier System. The aquifer between wells P-164 and P-145 exhibited less reducing condition than it should be because the pumping extraction drew more aerobic water from the fringe to the middle of the plume. The area influenced by these two pumping wells also exhibited a less degree of degradation, documented for example in well P-116, which was near the extraction well P-145.

This study provides information about the current degree of the biodegradation of chlorinated compounds in a fracture rock aquifer. This information is very valuable for the evaluation of natural attenuation as strategy for long term plume management or for

future remediation strategies such as biostimulation or bioaugmentation at the site. As part of future work, it is recommended to perform microcosm experiment to evaluate the limit factors that control the complete transformation of PCE and TCE to ethane. One of the unique findings of this study is that the current and long term behavior of the chlorinated compounds (degradation history) in the most contaminated hydrogeologic unit (Layer 5) has been mainly controlled by plume management strategies including DNAPL pumping in the source and the operation of a Hydraulic Barrier System. Hydrocarbons compounds, Ketones and BTEX acting as electron donors and carbon substrate for the microbial community were shown to have controlled the past and current redox conditions, thus the degree and potential of biodegradation of chlorinated ethenes and chlorinated ethanes at the site.

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Appendices

Appendix I Field Parameters

Field Sample ID	GeoTrans Layer Number	Depth to water (ft)	TOC elevation (ft)	Water level (ft)	Temperature (°C)	pH	EC (ms/cm)	ORP (mV)	DO (ppm)
MW-49R	1	6.51	868.06	861.55	14.4	7.2	0.4		
P-53	2	44.98	911.83	866.85	10.98	7.43	3.77	-117	0.57
P-94	2	1.45	860.25	858.80	15.08	8.06	0.727	0	1.45
MP-3-1	3				9.67	7.37	0.93		
P-157	3	0.46	860.39	859.93	12.05	8.06	0.751	2	1.92
P-151	3	0.88	860.39	859.51	10.86	8.21	0.839	97	0.99
MP-3-2	4				10.01	7.55	0.64		
P-95	4	0.24	860.49	860.25	11.55	8.05	0.783	-13	1.85
P-108	4	9.73	870.19	860.46	15.5	7.99	0.763	1	3.99
P-152	4	0.71	860.26	859.55	11.1	8.16	0.765	77	0.59
MP-3-4	5				10.07	6.84	1.52		
P-90	5	0.54	862.53	861.99	10.86	8.07	0.751	7	6.66
P-115	5	11	872.91	861.91	13.02	7.91	1.188	-142	0.49
P-71	5	15.75	877.54	861.79	14.75	7.88	0.726	163	0.91
P-70	5	6.19	869	862.81	12.4	7.93	0.656	105	8.14
P-164	5	36.61	874.64	838.03	12.2	7.18	0.37		
P-129	5	0.79	861.38	860.59	11.53	8.11	0.861	1	8.3
P-145	5	68.21	860.6	792.39	14	7.21	0.32		
P-156	5	-3	861.23	864.23	9.71	8.13	0.718	-53	0.49
P-116	5	-0.1	861.15	861.25	10.71	8.82	0.715	34	0.58

Field Sample ID	GeoTrans Layer Number	Depth to water (ft)	TOC elevation (ft)	Water level (ft)	Temperature (°C)	pH	EC (ms/cm)	ORP (mV)	DO (ppm)
P-131	5	11.26	873.03	861.77	11.77	8.12	0.66	-108	3.63
P-153	5	-2.5	860.07	862.57	10.33	8.2	0.747	-80	0.54
P-132	5	9.7	871.62	861.92	11.47	8.44	0.656	173	3.8
P-160	5	-3	860.44	863.44	10.77	8.17	0.675	204	0.82
P-136	5	-2.97	858.46	861.43	12.4	8.25	0.613	-36	7.02
P-140	5	13.7	874.55	860.85	13.82	7.99	0.639	-39	4.27
P-138	5	26.71	887.16	860.45	11.53	8.12	0.635	210	4.36

Bailer
Extraction wells
Westbay well
Flowing, assumed value

Field-measured parameters from September 2007. TOC is short for top of casing. Water level is calculated by subtract depth to water from TOC elevation. EC is short for electrical conductivity. ORP is short for oxidation reduction potential. DO is short for dissolved oxygen.

Appendix II Concentration of Inorganics

Sample ID	Layer Number	HCO3	Cl	SO4	Ca	Fe	K	Mg	Mn	Na	Si
MP-3-1	3	419	70	< 0.5	131	17.4	1.87	63.2	0.736	8.76	6.55
MP-3-2	4	322	15	1.5	82.2	2.34	0.56	40.0	0.288	3.20	6.31
MP-3-4	5	338	330	13	184	51.8	8.69	71.4	1.20	75.9	12.5
MP-6-17	6	377	1.2	9.1	77.7	< 0.01	1.79	49.1	0.003	3.69	6.71
MP-6-23	6	300	6.5	15	73.6	< 0.01	1.88	44.7	0.002	4.79	7.41
MP-6-27	5	293	15	19	78.7	< 0.01	1.71	44.9	0.001	4.66	7.24
MP-6-29	5	298	6.3	16	66.6	< 0.01	1.34	38.8	< 0.001	3.73	6.91
MP-6-30	4-5	280	3.7	11	59.2	< 0.01	1.00	35.1	0.001	2.59	6.26
MP-6-31	4	285	4.0	7.2	64.3	< 0.01	1.20	38.7	0.001	2.95	6.66
MP-6-37	3	285	23	18	80.1	< 0.01	1.53	45.3	< 0.001	4.84	7.85
MP-8-10	5	314	4.9	6.3	48.5	0.46	1.47	40.7	0.069	2.53	3.98
MP-8-11	4	353	1.0	6.8	49.5	0.12	1.43	51.6	0.452	19.5	5.58
MP-8-12	3	383	6.1	9.9	47.2	0.09	2.50	31.9	0.622	74.8	5.79
MP-8-3	6	361	0.9	< 0.5	69.0	3.30	1.63	51.3	0.021	4.18	6.34
MP-8-5	6	345	1.3	0.6	65.7	4.37	1.05	51.0	0.172	4.11	6.65
MP-8-7	6	320	0.6	< 0.5	54.1	5.48	1.31	49.2	0.078	3.05	6.60
MP-8-9	5	329	0.8	< 0.5	52.1	5.31	1.42	52.6	0.332	3.21	5.96
MW-49R	1	368	9.3	56	103	0.06	0.79	54.9	< 0.001	4.28	10.4
P-108	4	309	23	24	78.4	< 0.01	1.31	48.8	< 0.001	7.39	7.67
P-115	5	387	120	1.3	117	18.3	0.33	64.3	1.46	17.8	9.92
P-116	5	318	18	10	78.6	0.02	1.22	44.1	0.007	3.86	6.65
P-129	5	313	44	13	83.5	< 0.01	1.35	49.1	< 0.001	19.2	7.15
P-131	5	296	8.8	14	72.3	< 0.01	1.29	41.2	< 0.001	3.43	6.45
P-132	5	286	8.9	11	72.0	0.04	1.28	41.6	< 0.001	3.68	6.65
P-136	5	299	2.9	4.0	59.3	< 0.01	1.49	44.0	< 0.001	3.07	5.67
P-138	5	323	0.8	3.2	50.8	< 0.01	1.92	51.5	< 0.001	2.94	5.27
P-140	5	307	4.6	6.2	57.9	< 0.01	1.84	48.6	< 0.001	2.98	5.70
P-145	5	313	33	10	75.2	0.69	1.09	46.8	0.277	8.06	6.02
P-151	3	321	24	30	95.8	0.02	1.60	48.3	0.132	6.67	8.13
P-152	4	321	25	20	81.6	0.01	1.34	49.5	0.499	5.49	7.28
P-153	5	328	28	9.1	76.6	2.11	0.52	46.4	0.755	7.15	7.47
P-156	5	318	22	13	78.3	1.91	0.54	44.7	0.533	5.47	6.25
P-157	3	296	28	31	78.8	< 0.01	1.52	44.9	< 0.001	8.66	8.07
P-160	5	307	7.3	10	73.7	0.01	0.85	42.8	0.168	4.40	5.47
P-164	5	319	32	14	83.5	3.40	1.38	45.2	0.170	7.42	6.75

Sample ID	Layer Number	HCO3	Cl	SO4	Ca	Fe	K	Mg	Mn	Na	Si
P-53	2	767	470	< 0.5	411	259	4.48	167	0.956	30.3	11.3
P-70	5	302	6.4	11	69.3	0.02	1.07	42.3	< 0.001	3.53	6.47
P-71	5	299	15	17	78.1	0.02	1.50	42.5	0.002	4.99	6.36
P-90	5	343	18	9.3	74.3	< 0.01	1.53	50.8	< 0.001	10.3	6.46
P-94	2	309	27	29	73.6	< 0.01	1.37	42.0	0.001	8.33	7.88
P-95	4	299	29	30	80.6	< 0.01	1.35	46.2	< 0.001	8.57	8.14
Units		mg/L as CaCO3	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L

Appendix III Concentration of Chlorinated Ethenes and Dissolved Gases (UW)

	Sample Name		TCE (ug/l)	PCE (ug/L)		VC (ug/L)	11DCE (ug/L)	tDCE (ug/L)	cDCE (ug/L)		methane (ug/L)	ethene (ug/L)	Ethyne (ug/)	ethane (ug/L)
1	P-131		486.4	69		nd	188	nd	232		21.7	nd	nd	nd
2	P-136		6.6	1.4		nd	nd	nd	nd		13.8	nd	nd	nd
3	P-140		85.1	11.9		nd	nd	nd	27.5		28.4	nd	nd	nd
4	P-108		6.9	10.4		nd	nd	nd	nd		23.2	nd	nd	nd
5	P-157		37.3	35.6		nd	nd	nd	7.7		10.9	nd	nd	nd
6	P-94		31.5	32.3		nd	nd	nd	6.5		nd	nd	nd	nd
7	P-95		31.7	32.2		nd	nd	nd	7.3		nd	nd	nd	nd
8	P-129		11.4	2.5		nd	nd	nd	nd		nd	nd	nd	nd
9	P-90		nd	nd		nd	nd	nd	nd		nd	nd	nd	nd
10	FIELD BLANK		nd	nd		nd	nd	nd	nd		nd	nd	nd	nd
11	MP-8-10		55.5	7.4		nd	9.3	nd	20.2		144	nd	nd	nd
12	MP-8-9		nd	nd		nd	nd	nd	nd		222	nd	nd	nd
13	MP-8-3		3.5	1.1		nd	nd	nd	nd		876	nd	nd	nd
14	MP-8-5		9.5	1.5		nd	nd	nd	nd		475	nd	nd	nd
15	MP-8-7		3.3	1.2		nd	nd	nd	nd		247	nd	nd	nd
16	MP-8-11		1.4	nd		nd	nd	nd	nd		50.6	nd	nd	nd
17	MP-8-12		17.4	2.9		nd	nd	nd	11.1		54.5	nd	nd	nd
18	MP-3-2		nd	nd		nd	nd	nd	nd		81.4	237	nd	nd
19	MP-3-1		5.7	1.8		13.2	nd	nd	14.8		1861	1964	nd	nd
20	MP-3-4		125	977		1811	9912	59.2	14767		894	1395	nd	33.4
21	MW-49R		3	nd		nd	nd	nd	20.2		nd	nd	nd	nd
22	MP-6		nd	nd		nd	nd	nd	nd		nd	nd	nd	nd
23	MP-6-17		nd	nd		nd	nd	nd	6.9		nd	nd	nd	nd
24	MP-6-23		2.7	2.2		nd	nd	nd	nd		nd	nd	nd	nd
25	MP-6-27		1.7	1		nd	nd	nd	nd		nd	nd	nd	nd
26	MP-6-29		1.9	nd		nd	nd	nd	nd		nd	nd	nd	nd
27	MP-6-30		3.3	nd		nd	nd	nd	nd		nd	nd	nd	nd
28	MP-6-31		2.9	nd		nd	nd	nd	nd		nd	nd	nd	nd
29	MP-6-37		1.3	1.5		nd	nd	nd	nd		11.8	nd	nd	nd
30	p-53		38	3.2		16941	1251	nd	31280		11298	15646	nd	nd
31	p-70		1.3	1		12.8	nd	nd	38.1		27.4	28.5	nd	nd
32	p-71		13.2	4.3		nd	60.1	nd	499.3		15	nd	nd	nd
33	p-115		136	57.3		1932	1082	13.3	19129		272.9	436	nd	nd

	Sample Name		TCE (ug/l)	PCE (ug/L)		VC (ug/L)	11DCE (ug/L)	tDCE (ug/L)	cDCE (ug/L)		methane (ug/L)	ethene (ug/L)	Ethyne (ug/)	ethane (ug/L)
34	p-116		703	122		40.8	614	5.9	1439		11.9	nd	nd	nd
35	p-132		52.4	14.9		nd	103	nd	651		nd	nd	nd	nd
36	p-138		nd	nd		nd	nd	nd	nd		nd	nd	nd	nd
37	p-145		91.2	22.7		194	234	7.4	1600		37	62	nd	nd
38	p-151		37.5	4.9		nd	15.7	nd	40.2		nd	nd	nd	nd
39	p-152		51.9	18.4		79.7	137	3.7	1694		19.1	15.4	nd	nd
40	p-153		24.2	40.6		207	662	15.4	6618		178.7	73.1	nd	nd
41	p-156		25.2	14.7		338	477	8.8	4312		959	53.8	nd	nd
42	p-160		5.6	3.9		nd	43.9	nd	340		11.7	nd	nd	nd
43	p-164		43.7	24.7		268	523	3.1	5354		92.3	197	nd	nd
	Blank		nd	nd		nd	nd	nd	nd		4.6	nd	nd	nd
	MDL(ug/L)		0.6	0.9		1.3	3.9	2.3	1.9		0.5	0.5	3.1	0.4

Note: this analysis of concentration of chlorinated ethenes and dissolved gases was done at the Institute for Groundwater Research, University of Waterloo.

Appendix IV Concentration of Detected VOCs (GeoTrans)

Sample ID	111TCA	11DCA	11DCE	12DCA	2-Butanone	4-Methyl-2-pentanone	Acetone	Benzene	Chloroethane	cisDCE	Ethylbenzene	Methylene Chloride	PCE	Toluene	transDCE	TCE	VC	Xylene, Total
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
P-108	**2.9**	< 0.75	< 0.57	< 0.36	< 4.3	< 1.2	< 2.3	< 0.41	< 0.97	**4.6**	< 0.54	< 0.43	**11**	< 0.67	< 0.89	**10**	< 0.18	< 2.6
P-129	**31**	**1.9**	**3.1**	< 0.36	< 4.3	< 1.2	< 2.3	< 0.41	< 0.97	**31**	< 0.54	< 0.43	**2.5**	< 0.67	< 0.89	**15**	< 0.18	< 2.6
P-131	**740**	**7.6**	**100**	< 1.8	< 22	< 6.0	< 12	< 2.0	< 4.8	**240**	< 2.7	< 2.2	**77**	< 3.4	< 4.4	**540**	< 0.90	< 13
P-136	**7.1**	< 0.75	**2.8**	< 0.36	< 4.3	< 1.2	< 2.3	< 0.41	< 0.97	**2.4**	< 0.54	< 0.43	**0.75**	< 0.67	< 0.89	**8.1**	< 0.18	< 2.6
P-140	**84**	**5**	**20**	< 0.36	< 4.3	< 1.2	< 2.3	< 0.41	< 0.97	**39**	< 0.54	< 0.43	**11**	< 0.67	< 0.89	**97**	< 0.18	< 2.6
P-157	**4.8**	< 0.75	**2.3**	< 0.36	< 4.3	< 1.2	< 2.3	< 0.41	< 0.97	**11**	< 0.54	< 0.43	**36**	< 0.67	< 0.89	**42**	< 0.18	< 2.6
P-90	**1.4**	< 0.75	**1.8**	< 0.36	< 4.3	< 1.2	< 2.3	< 0.41	< 0.97	**1.8**	< 0.54	< 0.43	< 0.45	< 0.67	< 0.89	**0.72**	< 0.18	< 2.6
P-94	**2.5**	< 0.75	**1.9**	< 0.36	< 4.3	< 1.2	< 2.3	< 0.41	< 0.97	**6.3**	< 0.54	< 0.43	**33**	< 0.67	< 0.89	**34**	< 0.18	< 2.6
P-95	**3.4**	< 0.75	< 0.57	< 0.36	< 4.3	< 1.2	< 2.3	< 0.41	< 0.97	**7.9**	< 0.54	< 0.43	**30**	< 0.67	< 0.89	**31**	< 0.18	< 2.6
P-116	**1,200**	**410**	**290**	< 7.2	< 86	< 24	< 46	< 8.2	**30**	**1,600**	< 11	**12**	**130**	< 13	**19**	**840**	**29**	< 52
P-132	**420**	**11**	**50**	< 1.8	< 22	< 6.0	< 12	< 2.0	< 4.8	**610**	< 2.7	< 2.2	**15**	< 3.4	< 4.4	**50**	**0.97**	< 13
P-145	**720**	**660**	**150**	< 7.2	< 86	< 24	< 46	< 8.2	**39**	**2,000**	**13**	**9.6**	**24**	**42**	**21**	**110**	**210**	< 52
P-151	**32**	**11**	**7.7**	< 0.36	< 4.3	< 1.2	< 2.3	< 0.41	< 0.97	**34**	< 0.54	**0.57**	**5.7**	< 0.67	< 0.89	**41**	< 0.18	< 2.6
P-152	**860**	**460**	**120**	< 9.0	< 110	< 30	< 58	< 10	**30**	**2,200**	< 14	**17**	**26**	< 17	< 22	**67**	**97**	< 65
P-153	**4,000**	**900**	**490**	< 36	< 430	< 120	< 230	< 41	< 97	**9,400**	**130**	< 43	< 45	< 67	< 89	< 48	**230**	< 260
P-164	**670**	**4,000**	**370**	< 36	**1,600**	**740**	**2,600**	< 41	**210**	**7,300**	**170**	**840**	< 45	**2,000**	< 89	**49**	**300**	**640**
MP-3-1	< 9.0	**330**	< 5.7	**72**	**99**	**2,000**	**170**	**6.2**	**1,400**	< 8.3	**52**	**110**	< 4.5	**1,300**	< 8.9	**4.9**	**6**	**190**
MP-3-2	**4.8**	**61**	< 0.57	**1.8**	< 4.3	< 1.2	< 2.3	< 0.41	**1.4**	**1.7**	**0.8**	**1.3**	< 0.45	**45**	< 0.89	**2.7**	**13**	< 2.6
MP-3-4	**6,900**	**59,000**	**3,100**	< 360	**26,000**	**18,000**	**38,000**	< 410	< 970	**110,000**	**4,100**	**11,000**	**820**	**39,000**	< 890	< 480	**920**	**16,000**
MW-49R	< 0.90	**3.3**	< 0.57	< 0.36	< 4.3	< 1.2	< 2.3	< 0.41	< 0.97	**18**	< 0.54	< 0.43	< 0.45	< 0.67	< 0.89	**5.2**	< 0.18	< 2.6
P-115	**1,100**	**6,900**	**1,200**	< 90	**22,000**	**16,000**	**27,000**	< 100	**3,000**	**26,000**	**870**	**6,500**	< 110	**9,100**	< 220	**160**	**1,200**	**3,100**
P-138	< 0.90	< 0.75	< 0.57	< 0.36	< 4.3	< 1.2	< 2.3	< 0.41	< 0.97	< 0.83	< 0.54	< 0.43	< 0.45	< 0.67	< 0.89	< 0.48	< 0.18	< 2.6
P-156	**2,200**	**1,100**	**230**	< 14	< 170	< 48	< 93	< 16	< 39	**4,900**	**66**	< 17	< 18	**35**	< 36	**25**	**270**	**120**
P-160	**230**	**16**	**17**	< 1.4	< 17	< 4.8	< 9.3	< 1.6	< 3.9	**410**	< 2.2	< 1.7	**3.4**	< 2.7	< 3.6	**7.2**	< 0.72	< 10

Sample ID	111TCA	11DCA	11DCE	12DCA	2-Butanone	4-Methyl-2-pentanone	Acetone	Benzene	Chloroethane	cisDCE	Ethylbenzene	Methylene Chloride	PCE	Toluene	transDCE	TCE	VC	Xylene, Total
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
P-53	< 220	**19,000**	**1,000**	**610**	**52,000**	**70,000**	**65,000**	< 100	**3,100**	**32,000**	**600**	**1,200**	< 110	**24,000**	< 220	< 120	**16,000**	**1,900**
P-70	**7.5**	< 0.75	**0.79**	< 0.36	< 4.3	< 1.2	< 2.3	< 0.41	< 0.97	**13**	< 0.54	< 0.43	**0.78**	< 0.67	< 0.89	**1.9**	< 0.18	< 2.6
P-71	**180**	**37**	**18**	< 0.90	< 11	< 3.0	< 5.8	< 1.0	**3.6**	**340**	< 1.4	**2.9**	**5**	< 1.7	**4.1**	**19**	**6.6**	< 6.5
Units	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L

Note: numbers are bold if exceed the WI Public Health Groundwater Enforcement Standard. Totally 35 compounds were analyzed for each sample in Pace Analytical Services, Inc commissioned by GeoTrans but only 18 of them that were detectable at least in some of the samples were listed in this table.

Appendix V Carbon Isotopes Data

Chlorinated Ethenes

Field Sample ID	Layer	PCE		TCE		cis-DCE		1,1-DCE	
		$\delta^{13}C$	Conc.	$\delta^{13}C$	Conc.	$\delta^{13}C$	Conc.	$\delta^{13}C$	Conc.
MW-49R	1		0		3	-31.20	18		0
P-94	2	-29.25	32	-27.39	32		6		2
P-53	2		3		38	-15.06	32000	-10.33	1000
P-157	3	-29.58	36	-27.68	37	-25.43	11		2
P-151	3		5	-28.82	38	-24.87	34		8
MP-8-12	3		3	-25.65	17	-27.54	11		0
P-95	4	-29.62	32	-27.94	32		8		0
P-152	4	-23.59	18	-26.23	52	-25.58	2200	-19.63	120
P-108	4	-31.27	10	-28.99	7		5		0
P-71	5		4	-27.30	13	-26.80	340	-20.73	18
P-70	5		1		1	-28.04	13		1
P-164	5		25		44	-26.77	7300		370
P-160	5		4		6	-27.99	410	-22.01	17
P-156	5		15	-22.11	25	-25.79	4900	-21.65	230
P-153	5	-17.22	41	-14.71	24	-26.58	9400	-21.66	490
P-145	5	-23.94	23	-27.33	91	-23.52	2000	-18.61	150
P-140	5	-27.02	12	-27.74	85	-25.87	39	-23.78	20
P-132	5	-21.96	15	-25.98	52	-27.59	610	-23.03	50
P-131	5	-29.19	69	-28.51	486	-28.36	240	-25.69	100
P-129	5		3	-26.78	11	-28.23	31		3
P-116	5	-28.01	122	-28.50	703	-25.93	1600	-24.12	290
P-115	5		57		136	-26.64	26000	-20.60	1200
MP-8-10	5		7	-26.97	56	-26.03	20		9
MP-3-4	5		977		125	-27.84	110000	-28.67	3100

Note: $\delta^{13}C$ values are all expressed in the per mil form and the concentrations (in shaded columns) are all in the units of μg/L.

Chlorinated Ethenes

Field Sample ID	Layer	1,1,1-TCA		1,1-DCA		Chloroethane	
		$\delta^{13}C$	Conc.	$\delta^{13}C$	Conc.	$\delta^{13}C$	Conc.
P-53	2		0	-19.01	19000		0
P-151	3	-26.18	32		11		0
MP-8-12	3	-25.48	0		0		0
MP-3-1	3		0	-6.85	330		4
P-152	4	-24.91	860	-24.56	460		39
MP-3-2	4		5	-18.53	61		0
P-71	5	-25.16	180	-26.58	37		0
P-164	5		670	-25.56	4000		0
P-160	5	-25.62	230	-33.41	16		0
P-156	5	-26.32	2200	-28.42	1100	--	30
P-153	5	-25.80	4000	-28.93	900		0
P-145	5	-23.78	720	-24.15	660		30
P-140	5	-25.21	84		5		0
P-132	5	-26.01	420		11		0
P-131	5	-25.41	740		8		0
P-129	5	-25.16	31		2		0
P-116	5	-25.92	1200	-24.49	410		3000
P-115	5		1100	-19.05	6900		0
MP-8-10	5	-24.67	0		0		0
MP-3-4	5	-23.52	6900	-25.58	59000		3100

Note: $\delta^{13}C$ values are all expressed in the per mil form and the concentrations (in shaded columns) are all in the units of μg/L.