USING POSITIVE MATRIX FACTORIZATION TO INVESTIGATE MICROBIAL

DECHLORINATION OF CONTAMINANTS IN GROUNDWATER

by

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ABSTRACT OF THE DISSERTATION

USING POSITIVE MATRIX FACTORIZATION TO INVESTIGATE
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Monitoring data regarding aqueous groundwater concentrations of chlorinated benzenes,

chlorinated ethenes and halomethanes as well as ancillary parameters (such as

geochemical, nutrient and field data) have been collected from various wells at the

Chambers Works site for over two decades. In effort to make use of this investment we

applied a sophisticated statistical analysis to the data to elucidate evidence of potential

degradation processes that these chemicals may undergo in the subsurface. Halogenated

organic compounds are subject to various chemical, physical and biological forces and

can undergo chemical reactions and transformations. Positive matrix factorization (PMF)

was applied to the monitoring data onsite and has proven useful in characterizing

different locations and revealing microbial degradation processes resulting, in distinct

fingerprints for each organohalide family explored in this work.

PMF resolved three factors in the chlorinated benzenes (Chapter 2), chlorinated ethenes (Chapter 3), and halomethanes (Chapter 4) groundwater datasets. In Chapter 2, for the chlorinated benzene dataset, one factor represents a source of 1,2-dichlorobenzene and the other two factors represent dechlorination, where one factor represents a more advanced dechlorination regime than the other. In Chapter 3, for the chlorinated ethenes dataset, one factor represents a source of tetrachloroethene and trichloroethene. Of the three resolved factors in the chloroethenes dataset, two factors represent stages of dechlorination in which one factor represents a more advanced dechlorination regime than the next. Finally, in Chapter 4, PMF resolved three factors in the halomethane dataset where two factors represent sources of carbon tetrachloride and chloroform and one factor represents dechlorination.

ACKNOWLEDGEMENT

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1.1 Study Location

1.1.1 Background

This dissertation focuses on analysis of groundwater contamination data collected at the Chambers Works site in southern New Jersey. The Chambers Works complex was originally operated by the E. I. du Pont de Nemours and Company (hereafter referred to as DuPont). As of 2015, Chambers Works was transferred to the Chemours Company. It is located in Deepwater, Salem County, New Jersey and covers approximately 1,455 acres. The site is bordered to the west by the Delaware River, to the south by a canal, and to the east by recreational and residential areas (Figure 1-1).

Due to the long history of contamination at this site, a large database of measurements of contaminants, geochemical indicators, and other parameters in groundwater is available. The main goal of this research was to determine whether this existing database could be mined using factor analysis and other tools to yield information about pollutant degradation, without the need for expensive new data collection.

1.1.2 The Chambers Works Facility

Chambers Works started manufacturing chemicals in 1892 when a smokeless gunpowder plant was constructed there.[1] The production of organic chemicals commenced in 1917 and has continued to present day, with production of approximately 600 products including organic chemicals and organic intermediates, including refrigerants, stain

blocking agents, chemical intermediates, agricultural chemicals, and polymers.[1, 2] The site manufactured many well-known products throughout the past such as smokeless gunpowder, Freon®, and Teflon®.[1] Polymers, radiological materials, explosives, and dyes were also manufactured onsite.[1]

In early years, waste disposal consisted of a system of unlined trenches, into which waste was placed to flow downhill to a natural wetland area and later into a waste treatment plant. As a result, contaminants infiltrated into the groundwater and were not confined to a specific area onsite. There are several active waste-management areas onsite, including a secure landfill and a wastewater treatment plant.[1, 2] The wastewater treatment facility treats a maximum of 43 million gallons of wastewater per day and is operated under a permit issued from the United States Environmental Protection Agency (US EPA) and the New Jersey Department of Environmental Protection (NJ DEP).[2] Sources of wastewater fed into the plant include but are not limited to decontamination waters, contaminated groundwater, biosludges, and spent acids.[2]

The Delaware River and the Salem Canal are located adjacent to the site and are sensitive receptors to any contamination coming from the facility. In addition, wetlands and a wildlife habitat area are located on the northern portion of the site. Air, soil, groundwater, and surface water contamination have been identified at the site in the past. Organic and inorganic constituents (and historically radiological materials) have been identified as onsite contaminants.[2, 3] The groundwater is contaminated with volatile organic compounds (VOC), semi-volatile organic compounds (SVOC), and heavy

metals.[2, 3] The organic contaminants of concern at the site include chlorinated

ethenes (CE), chlorinated benzenes (CB), aniline, para-chloroaniline, nitrobenzenes,

halomethanes (HM), and perfluorinated compounds, although many other compounds are

present in the subsurface.[2]
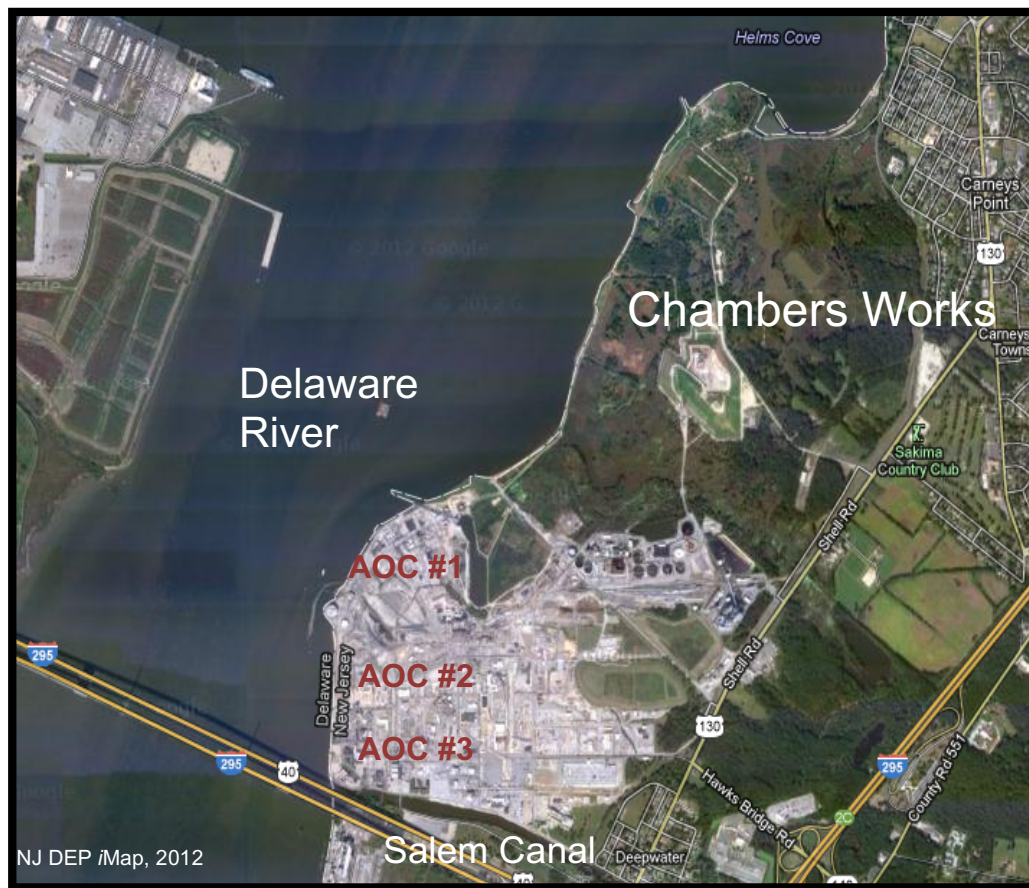
Figure 1-1. Site location map including select Areas of Concern (AOCs) at the Chambers Works facility located in Deepwater, New Jersey.

1.1.3 Environmental Remediation at Chambers Works

The Chambers Works Complex has a long history of remedial actions under oversight by the NJ DEP, US EPA Region II, and the Department of Health.[1] A Formerly Utilized Sites Remedial Action Program (FUSRAP) area is also located at Chambers Works.[1, 2] Remedial activities involving the US Department of Energy (US DOE) in accordance with FUSRAP took place in the late 1940s when uranium contaminated soil was excavated and removed from the site.[1, 2] Follow-up remedial activities were completed in 2005 to ensure compliance with current US DOE guidelines.[1, 2] Follow-up activities involved a site-wide radiological survey, excavation and removal of contaminated soil, the decontamination and demolition of building 845, and the installation of soil caps in specified regions.[1, 2] A number of other remedial activities have taken place in the past to ensure compliance with the NJ DEP and US EPA regulations.

Three basins and two ditches were closed in the early 1990s, when two rounds of site-wide investigations took place.[2, 3] After the investigation, site personnel also excavated contaminated soil in the immediate area of an out-of-service landfill.[2, 3] Caps were installed over the land and fences were erected around the perimeter to contain the contaminated area.[2, 3]

In 1970, groundwater contamination was detected at the site perimeter, which prompted site personnel to install a groundwater recovery system to stabilize the groundwater plume. As a result, the site was designated a groundwater Classification Exception Area

(CEA). In order to restrict off-site migration of contaminated groundwater, the site also has permits requiring groundwater quality monitoring and as well as recovery programs (Permit No. NJ0083429 and NJ0105872).[3] Groundwater migration is controlled via two approaches: a pump and treat system and a barrier consisting of a slurry wall and sheet pile barrier. The combination of the said approaches hydraulically contain groundwater flow from entering surface water bodies by diverting flow to nearby interceptor (pumping) wells.

In February 2010 the pump and treat system pumped about 1.0 million gallons per day of contaminated groundwater to the wastewater treatment plant.[2, 3] The contaminated groundwater is treated onsite and discharged into the Delaware River after meeting acceptable water effluent quality standards.[2, 3] The slurry wall and sheet pile barrier were installed in the northwestern section of the site located adjacent to the Delaware River as well as adjacent to the Salem Canal in the southeastern portion of the site.[2, 3] As a result of the ongoing remediation activities and the operation of the interceptor system, impacted groundwater has been effectively contained on the site.

In summary there are three groundwater recovery systems operating onsite and six monitoring programs active onsite.[3] A total of 96 active monitoring wells throughout 16 unique Areas of Concern (AOC) are routinely sampled for various VOCs, SVOCs, and heavy metals in groundwater as well as ancillary field parameters such as temperature, dissolved oxygen, pH, nutrients, and redox indicators.[3] The goal of this work was to develop a method to demonstrate where, when, and under what conditions microbial degradation of contaminants is occurring, ideally without expensive new data

collection.

1.1.4. Microbial Dehalogenation

Organohalides comprise some of the main contaminants of concern in the groundwater at Chambers Works. Organohalide compounds are defined as an organic compound containing one or more substituted halogen atoms. They can be biotransformed or mineralized in the subsurface by microorganisms via aerobic or anaerobic dechlorination mechanisms. Since this work mainly focuses on organohalide contaminants in the groundwater at Chambers Works, anaerobic reductive dechlorination is one of the most relevant mechanisms of degradation. Further information regarding dechlorination mechanisms of chlorobenzenes, chloroethenes and halomethanes are found in Chapter 2, Chapter 3, and Chapter 4, respectively.

1.1.4.1 Evidence of Microbial Dechlorination Onsite

Multiple studies have found the potential for microbial degradation of chlorobenzenes (pentachlorobenzene, tetrachlorobenzenes, trichlorobenzenes, and dichlorobenzenes, and monochlorobenzene) in laboratory microcosms using sediment that was collected at the site.[4-9] Similarly, chloroethene (tetrachloroethene, trichloroethene, dichloroethene isomers, and vinyl chloride) degradation has been shown in laboratory microcosm studies using sediment from the site.[4, 10, 11] In 2014, a recent study by Nelson *et. al.*[4] did not see dechlorination of halomethanes (chloroform and dichloromethane) by *Dehalobacter* strains -12DCB, -13DCB, and -14DCB, isolated from this site, however, halomethane dechlorination has recently been observed by *Dehalobacter* strains RM1

and Dhb-CF (not isolated from this site[12, 13]) in laboratory microcosm experiments.

1.2 Groundwater at Chambers Works

Over 300 wells have been installed at the subject site throughout the past, which include

monitoring wells, piezometers, recovery (pumping) wells, and interceptor wells. Certain

wells are routinely sampled for specified compounds and field parameters in order to

comply with multiple NJ DEP groundwater monitoring programs. The Chambers Works

complex contains both widespread and localized areas of subsurface contamination,

depending on the contaminant class. The site is split into various AOCs, reflecting the

availability of groundwater data concerning specific classes of compounds measured in

sets of monitoring wells located throughout the site. Five aquifers (i.e., from top to

bottom Aquifers A, B, C, D, and E) have been identified underlying the site, and wells

have been installed and screened at appropriate depths to monitor the groundwater in

each aquifer[2, 3]. The site's hydrogeology is further explained below. Datasets

containing site-wide aqueous phase groundwater contaminant concentrations measured in

all of the aquifers were used in this work; however, the majority of the data comes from

the B aquifer. It should be noted that monitoring wells are screened at different intervals

and groundwater samples may be collected over 5 to 10 feet below ground surface. The

samples collected represent multiple stratigraphic layers and contain various ecological

niches that may reflect different activities as well as different redox characteristic,

especially for different wells.

1.2.1 Hydrogeology

The site is located in the southwest climate zone in New Jersey, and is underlain by approximately 500 feet of unconsolidated Coastal Plain sediment deposited during the Holocene epoch.[2, 3] Five aquifers have been identified onsite (i.e., Aquifers A, B, C, D, and E). [2, 3] The A-aquifer is an unconfined unit composed of mainly fill material and ranges from 0 to 17 feet thick across the site.[2, 3] Much of the groundwater contamination is found throughout the B-aquifer, which is a semi-confined system composed of clay, silt, and sand ranging from 15-20 feet thick.[2, 3] The confining layer separating aquifers A and B is composed of silt, clay, and peat and ranges from 0 to 5 feet deep along the southeastern portion of the site.[2, 3] A discontinuous clay lens is found in the middle of the B-aquifer on the southeastern portion of the site, which separates the aquifer into an upper and lower section.[2, 3] The upper B-aquifer is composed of silty sand, whereas the lower B-aquifer is composed of sand and gravel.[2, 3] The B/C confining unit is a continuous layer of clay and observed at approximately 25 feet below ground surface.[2, 3] The bottom of the C aquifer varies in depth up to a maximum of 40 feet and is mainly composed of coarse-grained sand with some cobbles. [2, 3] The C/D confining unit separates the C-aquifer and the D-aquifer and is a continuous layer of clay to fine silt and observed at approximately 35 feet below ground surface.[2, 3] The D-aquifer is observed at approximately 35 feet below ground surface and mainly composed of coarse-grained sand with some cobbles.[2, 3] The D/E confining unit is a continuous layer of clay and observed at approximately 60 feet below ground surface.[2, 3] Finally, the E-aquifer is composed of sand, silt, and clay and the depth to which it is observed is unavailable.[2, 3]   It is important to note the site contains complex hydrology due to

engineering controls that are in place. Pumping and interceptor wells located in the south and southwestern areas of the site impede the natural flow of the groundwater throughout the various aquifers. It should be noted that the groundwater pumping regime has changed over time. Again, the pumping and interceptor wells stabilize groundwater contaminant plumes, thus preventing offsite migration.

1.2.2 Relevant Areas of Concern (AOC)

Chlorinated benzene groundwater contamination is ubiquitous throughout the site, whereas chloroethene and halomethane contamination is more localized. Some areas of chloroethene and halomethane contamination are attributed to use at that location onsite, whereas contamination observed at other areas is attributed to transport by advection due to groundwater flow. Below outlines specific AOCs associated with chloroethenes and halomethanes, as chlorinated benzene contamination is widespread across the site.

- Fluorinated products such as Freon 113 (CFC-113), which was manufactured by reacting an organic compound with hydrofluoric acid in the presence of a catalyst.[3] Commonly used organic compound in this process were carbon tetrachloride (CT), chloroform, and tetrachloroethene (PCE), which account for their presence and distribution near the Fluoroproducts area (AOC #1), which occupies approximately 52 acres in the west-southwestern portion of the site adjacent to the Delaware River (Figure 1).[3] The area also contains a historic outfall to the Delaware River. Freon 113 is a versatile solvent, which was mainly used as a cooling agent in refrigerants. The production of fluorinated products commenced in 1930 with the manufacture of Freon 113, which continued until the late 1980s.[3] The onset of the Montreal Protocol called for Freon 113, along

with other structurally similar chlorofluorocarbons, to be phased out due to its persistence in the atmosphere and its potential to cause ozone depletion. Although the production of Freon 113 ceased in the late 1980s, other fluorinated alkanes (e.g., fluorinated methanes, fluorinated ethanes, and fluorinated propanes) are still being manufactured in the area. These compounds have less potential (or no potential) to cause ozone depletion once released to the environment.[14] Some recently manufactured compounds in the Flouroproducts area include Zyron mixtures -116, -23, -8020, which are used as electronic gases, and refrigerants and fire suppressants such as SUVA® 95 (HFC-23/PFC-116), Freon 23 (HFC-23), and apaflurane (HFC-227). [3]

- Chlorinated ethenes (e.g., PCE, TCE, & VC) also appear in AOC #2, which encompasses 38.5 acres and is also known as the TEL (tetraethyl lead) area. The TEL area is located directly south of the Fluoroproducts area and is bordered to the west by the Delaware River. The area was historically used to produce motor fuel compounds such as tetraethyl lead, tetramethyl lead, trimethylethyl lead, 1,2-dibromoethane, 1,2-dichloroethane, and red dye between the years 1925 and 1975. A chloroethane (ethyl chloride) aboveground storage tank facility, or AST farm, as well as railroad loading and unloading area formerly occupied the area in the northwestern corner. Chloroethane was once used in producing tetraethyllead (TEL), an anti-knock gasoline additive. The area is also referred to as "anti-knocks" by site personal. The area had former process wastewater ditches and miscellaneous releases near historic building facilities. The area likely contains CEs due to transport from other contaminated areas onsite such as AOC #1 and

AOC #2, which border the land to the north and south. Ditches A, B, and C were associated with the historic process waste system for the southern portion of the site. In addition to the remediation of Ditch A, B, and C, which was completed in 1996, the facilities in the TEL area were decontaminated and demolished between 1991 and 2001. Current site use in the immediate area is limited at the time, as most of the remaining overlying infrastructure is abandoned.

- The Jackson lab area (AOC #3) also contains elevated chlorinated ethene contamination and is located directly to the south of the TEL area (AOC #2). The Jackson lab area is located in the southwestern portion of the site covering approximately 32 acres. Synthetic indigo dye was manufactured between 1917 until the early 1970s in the northwestern portion of AOC 3.[3] The southwest portion of AOC 3 historically housed laboratory research and development facilities adjacent to the Delaware River and Salem Canal. Several research and development buildings were decontaminated and demolished between 1990 and 2000. In addition, a sheet pile barrier was installed in 2008 along the Salem Canal in to minimize contaminated groundwater discharging into the canal. Throughout the years of operation, research facilities in the Jackson Lab area had tested virtually every chemical used or produced onsite.[3] Products developed by the laboratory research facilities including dye formulations underwent process development and small-scale production within an operation called Semi-Works, which commenced in the early 1920s.[3] Semi-Works in AOC 3 is currently operating and produces chemical intermediates used in the onsite manufacturing of elastomers.[3] Current sources of chlorinated ethene contamination in the

aforementioned AOCs include residual constituents in former ditches as well as

DNAPL contamination in the subsurface near former ditches or process building

trenches.

1.3 Investigated Analytes

1.3.1 Organohalide Groundwater Contaminants

Chlorinated benzenes, chlorinated ethenes, and halomethanes are the main organic

contaminants detected in the subsurface at the former Chambers Works facility. Here we

investigate the aforementioned classes of compounds as well as their prospective break

down products in the groundwater. Information regarding the physical-chemical

properties of the investigated classes of chemicals, as well as their aqueous phase

groundwater concentrations and methods of measurement are further discussed in

Chapter 2 (chlorobenzenes), Chapter 3 (chloroethenes) and Chapter 4 (halomethanes) of

this work.

1.3.2 Ancillary Measurements

Ancillary parameters investigated in this work include temperature (T), pH, oxidation-

reduction potential (redox), dissolved oxygen (DO), alkalinity (ALK), total organic

carbon (TOC), total dissolved solids (TDS), nitrate (NO_3^-), nitrite (NO_2^-), sulfate (SO_4^{2-}),

sulfide (S^{2-}), methane (CH_4), ferric iron (Fe^{3+}), and ferrous iron (Fe^2). These parameters

can be used as indicators of the geochemical environment including redox state in the

subsurface.

1.3.2.1 Methods of Ancillary Measurements

There are issues regarding the availability and quality of concentration data of the investigated analytes and ancillary parameters. In many cases there was not a sufficient amount of samples in which both the contaminants and the ancillary parameters were measured. Environmental samples are already inherently complex and extracting samples at historically contaminated sites can yield a chemical stew. Even a straightforward environmental laboratory measurement can be confounded by one of the many the difficulties presented at the site. Since many of these redox species are transient in the environment (e.g., ferric iron and methane) gauging representative samples at greater depths can be a difficult task if proper sampling techniques are not implemented such as low-flow sampling methods.[15] Although temperature and sometimes pH field measurements can be adequately gauged using hand-held probes; Eh and DO are many times subject to error. [15] Measuring these parameters by this method can lead to incorrect results due to oxygen contamination and insufficient calibration during its lifespan.[15] For these reasons, it is important to investigate a broad range of redox indicators and not rely too heavily on any one type of measurement.

For these reasons, an additional ancillary parameter was investigated: the fraction of aniline as the sum of aniline and nitrobenzene (%AN) is also used here as an independent redox measurement. Nitrobenzene is rapidly transformed to aniline under reducing conditions[16, 17] and aniline and nitrobenzene are measured using similar (and sometimes the same) methods as the other organic contaminants such as chlorinated benzenes. Therefore matrix effects and data management issues are the same for the

nitrobenzene and aniline as for the other analytes, allowing more confidence in the

correlations between them. Further, there are a larger number of data points available for

the correlations with %AN. Statistical significance tests and p-values were calculated

between this parameter and other ancillary measurements. %AN is an independent redox

measurement, as it does not correlate with any other ancillary measurement. Despite

these advantages, it should be noted that laboratory measurements of aniline can also be

problematic. Aniline has a low pK_a value ($pK_a = 4.87$) and can undergo many acid/base

reactions as well as sorption and electrostatic interactions. At high concentrations, it is

likely the compound will sorb onto glassware and even chromatographic columns, which

will cause difficulty in the applied analytical method.

Specific issues with the various methods are noted below.

- In 1991, method 8270 began to be used for aniline and nitrobenzene. Method 625

  and 8270 were used to measure the aniline and nitrobenzene in 1993 at different

  locations onsite. Both method 625 and 8270 analyze for extractable semi-volatile

  organic pollutants in solid waste, soil, water, and air matrices using GC/MS and

  the main difference between the methods is that method 625 has shorter list of

  target analytes. Method 625 was required to be used in certain well locations in

  order to comply with NPDES, where federal regulations specify analytical

  methods for certain organic chemicals in industrial wastewater. As time

  progressed, various revisions of method 8270 were applied to measure the

  compounds. Method 8270A was used in 1994 and from 1995 to 1997 method

  8270B was used. For the next decade (1998-2008) method 8270C was used to

measure aniline and nitrobenzene and in 2009 methods 8270C and 8131 were both used. Method 8131 outlines the analysis of aniline and selected derivatives of aniline by GC and a specific detector. From 2009 to present, method 8270C has been used to measure the nitrobenzene and method 8131 is currently used for aniline. The frequent change in the methods for aniline is not surprising since measuring aniline can be challenging.

- Temperature, redox, and pH were measured in the field with handheld probes. Laboratory pH measurements were infrequently reported. Field measurements were performed on grab samples extracted with Teflon bailers using electronic handheld probes. No formal field methods are reported between 1990 and 2007 and from 2008 to present day method STD-3WP is reported. Laboratory measurements of pH have been analyzed in samples by method 150.1 in the mid-1990s up until 2008 where method SM 4500-H+B began to be used.

- Data regarding redox indicators of subsurface conditions (ferric and ferrous iron, nitrite, sulfate, sulfide and methane) are present in the database since the early 1990s. Methane was measured using method D2820 in the early 1990s until 2005, after which method 8015B was used. Nitrite was measured using method 353.2 since the early 1990s and in 2004 was measured by method 300.0 in select wells screened at greater aquifer depths (i.e., aquifers C, D, E & F). EPA method 353.2 analyzes for nitrate and nitrite by automated colorimetry, whereas method 300.0 determines inorganic ions by ion chromatography. Method 300.0 was probably used to overcome interferences such as elevated contaminant levels. Ferric iron has been measured since 2009 using a modified method 6010B.

Ferrous iron has been measured by method SM 3500-Fe B since 2009. EPA method 6010B uses inductively coupled plasma-atomic emission spectrometry to determine trace metals in solution, while method SM 3500-Fe B (phenanthroline method) is a less sophisticated, colorimetric approach. From the early 1990s until 2008 sulfate and sulfide were measured using methods 375.4 and 376.1, respectively. Method 375.4 is a turbidimetric analysis using a spectrophotometer for detection and method 376.1 is a titration analysis. Methods 300.0 and SM 4500-S2 D (methylene blue method, colorimetric analysis) have measured sulfate and sulfide, respectively, from 2008 through 2011.

- Additional supplementary measurements include nutrients such as alkalinity and total organic carbon, which have been measured since the early 1990s and are both relatively straightforward measurements. Alkalinity (as calcium carbonate) is measured by titration to pH 4.5 and was analyzed using method 310.1 in the early 1990s-2008 and method SM 2320B after 2008. Total organic carbon was measured using methods 9060, 415.1, and 415.2 between 1990 and 2008. Method 5310C and 9060 have been used interchangeably from 2008 until present day. The methods cover the determination of TOC in drinking and source waters using a total organic carbon analyzer, and differ by the method of organic carbon oxidation and signal detection. Methods for TOC appear to vary by location throughout the site, perhaps due sample concentration ranges and sorption interferences.

1.4 Database

As previously mentioned, an environmental monitoring system has been in use for decades at Chambers Works. As the years proceeded, monitoring data was compiled and organized in the form of a Microsoft Access, Envista database for Microsoft Windows. The Envista database contains field survey data collected by field technicians and laboratory data measured by onsite and offsite New Jersey certified laboratories. The Envista database contains over two decades of data concerning contaminant concentrations measured in the surface water, groundwater, and soil as well as ancillary field parameters gathered during field sampling events. Each record includes GPS coordinates of the sampling site, the date the sample was taken, sample identification numbers, the sample matrix, units of concentration, method detection limits, practical quantitation limits, EPA qualifiers, as well as indicators and field parameters measured during sampling events.

1.5 Factor Analysis

1.5.1 Source Apportionment Tools

This work attempted to parse data from the Envista database using factor analysis. There are a number of specific factor analysis approaches that have been developed over the years. One of the simplest is Principle Components Analysis (PCA), which can be coupled with Multiple Linear Regression (MLR) to derive the strength of each Principle Component in each sample. More sophisticated methods include Polytopic Vector Analysis and Positive Matrix Factorization (PMF).

Only limited investigations have used simple factor analysis tools such as principal components analysis to describe groundwater data sets. PCA has been used to investigate data sets on concentrations of both naturally occurring elements and contaminants in groundwater. For example, some investigations have focused on identifying hydrologically connected units by examining the variations in concentrations of naturally occurring species such as major ions (i.e. nitrate, ammonium, sulfate etc.).[18, 19] Others have examined data sets which combine major ions with contaminants to answer questions about the number of sources and their fingerprints and to apportion responsibility for cleanup of contaminated groundwater.[18, 20] These investigations often focus on contamination by metals.[21, 22] While metals may change speciation, they cannot be degraded. Thus total metal (for example, total As) is conservative, which greatly simplifies the data analysis.

PCA has also been used to examine possible degradation of organics in groundwater, but these studies have focused primarily on the chlorinated ethenes[23, 24], since these are some of the most common groundwater contaminants. For example, Mathes and Rasmussen[24] used principal components analysis to analyze the data sets on groundwater parameters measured at the Savannah River site in South Carolina, USA. Their data set consisted of nearly 4,000 observations of pH, total dissolved solids, aluminum, calcium, chloride, iron, potassium, magnesium, sodium, silicon, sulfate, tritium, and tetrachloroethylene measured from 1993 to 1995.[24] Because their data set did not include products of dechlorination, they were not able to elucidate dechlorination pathways. However, the factor containing both tetrachloroethylene and chloride was

thought to likely be representative of degradation. Baek and Lee[23] conducted source apportionment of a plume consisting of dichloroethene and carbon tetrachloride in groundwater and industrial facility in Korea. Again, their data did not include products of dechlorination of these chlorinated solvents, so they were not able to determine pathways or the extent of degradation. Both of these investigations relied on principle components analysis (PCA).

Other researchers have investigated the application of a more sophisticated factor analysis tool to environmental data. Positive Matrix Factorization (PMF) is a receptor model that strives to estimate profiles of unknown sources, which may exist currently or have existed in the past. The PMF approach has been widely used to identify and quantify source contributions of aerosol particles (e.g., $PM_{2.5}$ and PM_{10} e.g.) and volatile organic compounds (VOCs)[25-28] in the atmosphere. Other work [29-39] involved the application of PMF to investigate source contributions of VOCs and semi-volatile organic compounds (SVOCs) in sediment, surface waters, and biota. Recently, Shao *et. al*.[32] applied PMF 3.0 (US EPA PMF version 3.0) to investigate the spatial distribution of 16 polycyclic aromatic hydrocarbons (PAHs) in topsoil, suspended solids and groundwater of a karst water resource in Shanxi Province located in northern China. Source profiles were identified as oil, coal combustion, vehicular, biomass combustion, as well as coke tar.[32] Although factors representing degradation were not identified, a bacterial strain capable of degrading low molecular weight PAHs (e.g., fluorene, phenanthrene, and pyrene) was later isolated and identified from the aquifer.[40]

In this investigation, we have utilized PMF to analyze the Chambers Works groundwater data. Due to the complexity of the Chambers Works site and of the monitoring data, a simple factor analysis tool such as PCA is not likely to be effective at apportioning sources and potentially revealing evidence of degradation in the subsurface. PMF is an advanced factor analysis method developed by Paatero and Tapper.[41] PMF has two major advantages over PCA. First, PMF uses uncertainty estimates for individual values to weight the data, which are usually based on surrogate recoveries or other analytical parameters. This provides a means for including species with missing values and data below detection limits; these are assigned a higher uncertainty so that they are down-weighted and have less influence on the solution. The second advantage is that PMF imposes a non-negativity constraint on the factor analysis solution. In contrast, PCA often generates negative source contributions that are not physically meaningful.[42] PCA sometimes identifies negative source contributions in response to extreme or outlier data values, a symptom of the "nonrobustness" of PCA.[42]

1.5.2 Positive Matrix Factorization (PMF)

PMF was applied to identify source profiles in the chemical monitoring data collected at Chambers Works over the past two decades. Details of this method have been presented elsewhere.[41, 43, 44] Briefly, the PMF model resolves the sample matrix (X) as product of two factor matrices (G and F) and a residual matrix (E):

$$X = GF + E \qquad\qquad \text{(Eqn. 1-1)}$$

The sample dataset is viewed as a matrix X of m by n dimensions, in which m is the number of analytes and n is the number of samples. The F matrix of m by p dimensions

describes the chemical profiles of a number of p factors or sources. The G matrix of p

by n dimensions describes the mass contribution of each factor to a given sample. The

goal of PMF is to optimize the number of factors p, and find the source profile matrix F

and the source contribution matrix G that result in minimizing the error.

The solution of PMF analysis is obtained by minimizing the sum of the weighed squared

residuals that is the Q value as described in Eqn. 2.

$$Q = \sum_{i=1}^{m} \sum_{j=1}^{n} \left(\frac{e_{ij}}{s_{ij}}\right)^2$$
(Eqn. 1.2)

where e_{ij} is the residual of the ith chemical species measured in the jth sample; and s_{ij} is an

estimate of the uncertainty in the ith chemical species measured in the jth sample.

1.5.3 PMF Software Versions

There are multiple versions of the PMF software available. Again, in 1994 Paatero and

Tapper[41] developed the original mode, PMF2, and the US EPA released three new

versions in recent years (i.e., PMF 3.0, PMF 4, and PMF 5.0). Recently, PMF2 and PMF

3.0 were compared in an investigation of sources of polychlorinated biphenyls (PCBs) in

air monitoring data in Chicago.[33] Shortly after, PMF2 was shown to better apportion

sources of PCBs and polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs) in the

Portland Harbor when compared to PMF 5.0.[45] Discrepancies have been found

between PMF2 and the EPA PMF versions, which include different algorithms used to

solve the model and non-negativity constraints, differences in handling rotational

freedom, as well as differences in the robust mode and handling of outliers.[33] For the

aforementioned reasons, PMF2 was selected as the model version appropriate for

apportioning environmental monitoring data of halogenated organic compounds and was thus used in our investigation.

1.5.4 Identifying the Correct Number of PMF Factors

The PMF2 model, like other factor analysis methods, cannot unequivocally indicate the correct number of source profiles needed to describe the dataset. The user must exercise his/her judgment in choosing the correct number of factors. The interpretability of the PMF results depends on selecting the 'correct' number of factors. Here, we present certain guidelines used to inform decisions regarding the correct number of factors in each data subset.

A Multiple Linear Regression (MLR) of the G matrix versus the sum of the analytes in each sample is a good indicator of the correct number of factors.[33] Since each additional factor must contribute in a positive and statistically significant way into the overall solution, the MLR indicates when factors have been generated that do not contribute positively and significantly to the overall solution, i.e. too many factors have been requested. A MLR of the G matrix versus the sum of the measured concentrations of the analytes should show all factors with positive and significant ($P < 0.05$) coefficients. The stability of model is also a good indicator the model has converged on a solution.[33] Model stability is gauged by computing the average relative standard deviation (RSD) of both the G and F matrixes. The PMF model was always run starting at 10 different initializing points, i.e., changing the seed values from 1 to 10, in order to evaluate the consistency of the model results. In some cases, the average relative

standard deviations of the results of these 10 model runs were large, sometimes in excess of 100%. Thus one criterion used to judge the correct number of factors was an acceptable low value of the average RSD of the G and F matrixes. [33]

In addition, the interpretability of factors is often regarded to better inform decisions since the factors generated by the PMF program should have physical meaning and be interpretable.[33] Plots of modeled versus measured concentrations should show good agreement between model output and the input data, as indicated by slope and R^2 values close to 1.[33] Increasing the number of factors will always serve to increase the agreement between modeled and measured concentrations, so this indicator is used only to confirm that the data set can be reasonably well simulated by the number of factors chosen. Lastly, plots of calculated and theoretical Q value versus number of factors are examined. The calculated Q value varies with the number of factors. [33] In theory, the calculated Q should be equal to the theoretical Q when the correct number of factors has been chosen. However, in many cases, especially when the error of measurement cannot be correctly estimated, the calculated Q value may deviate substantially from the theoretical one.

1.6 Challenges and Limitations

1.6.1 Physical Parameters of Groundwater System

Although PMF was originially designed to examine atmospheric contaminants such as fine particulate matter[30], its application to other environmental compartments,[31, 32, 34-36, 46], has gained popularity over the years. PMF has been used to investigate the

sources of SVOCs such as PCBs and brominated diphenyl ethers (BDEs) and PCDD/Fs in sediment and surface waters.[34, 36-38, 45-56]   One goal of this work is to determine whether PMF can be successfully applied to groundwater monitoring data in order to investigate microbial dehalogenation at Chambers Works. Analyzing groundwater contamination data is complicated by the variety of oxic and anoxic environments with potentially differing pathways, limited mixing of the water, and longer residence times when compared to surface water sytems.[14] Limiting mixing in the system is a result of impeded hydraulic connectivity in the horizontal and vertical dimensions, as well as anisotropy of hydraulic conductivity. Another issue arising from the nature of the contaminant class in the subsurface is the *chromatographic effect* on chlorinated organic compounds as they flow through the aquifer.[20] Many SVOCs that are classified DNAPLs will sorb to the aquifer solids at varying degrees, retarding their flow relative to the groundwater. This allows less hydrophobic compounds such as VC to migrate further and faster than the parent compounds that are more hydrophobic (i.e. PCE and TCE).

1.6.2 Quality of Groundwater Monitoring Data

In addition to difficulties which arise from the physical parameters of the system and the physico-chemical properties of the compounds of interest, there are other serious challenges associated with using PMF on the groundwater data from Chambers Works that are related to data collection and management. These include the application of different analytical methods, where different sample collection, preparation and instrumental techniques have been used throughout the years. Consequently, method detection limits (MDLs) vary across samples and not all of the analytes were measured in

each sample. Lastly, a comprehensive account of the chemical releases onsite is not known. Knowledge of the chemicals that were released, when they were released and where, onsite, would be advantageous, but this information is unavailable.

1.7 Outline of Dissertation

Microbial dechlorination of chlorinated solvents has been widely studied, however much of this research is focused on laboratory studies. These three chapters were designed to introduce an innovative data mining approach using PMF to investigate microbial degradation in groundwater under site-specific conditions. We have chosen the PMF model due to its successful source apportionment over wide range of environmental compartments including air[25, 26, 33, 57-59], surface waters[29, 56], sediment[31, 34, 50, 51, 60], and most recently, biota[35] and groundwater[32]. Aqueous phase groundwater monitoring data regarding three distinct classes of halogenated organic contaminants are investigated. Therefore, this dissertation is includes three separated parts investigating microbial degradation of chlorobenzenes (Chapter 2), chloroethenes (Chapter 3), and halomethanes (Chapter 4) in the groundwater at the former Chambers Works site. These chapters will explore the following questions:

1. Can PMF analysis be successfully performed on data of this quality?
2. Can PMF analysis indicate where, when and under what conditions microbial dechlorination of contaminants is occurring in the groundwater at Chambers Works?

3. Can the answers to question 2 indicate any practical approaches that the operators of Chambers Works could use to enhance the natural dechlorination occurring at their site?

4. What can this data mining exercise tell us about the quantity and quality of data needed to answer questions 1 through 3? Can we make recommendations about how data collection and management should be conducted in the future to aid data mining efforts?

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Chapter 2: Chlorinated Benzenes

Abstract

Chlorinated benzenes are common groundwater contaminants in the United States, and demonstrating whether they undergo degradation in the subsurface is important in determining the best remedy for this contamination. The purpose of this work was to use a new approach to investigate chlorinated benzene degradation pathways in the subsurface. Positive Matrix Factorization (PMF) was applied to historical monitoring data regarding chlorinated benzenes measured in groundwater at the DuPont Chambers Works facility, Deepwater, NJ. A dataset containing 597 aqueous groundwater samples and 5 chlorinated benzenes and benzene collected from approximately 140 wells over 20 years was investigated using PMF2 software. Despite the shortcomings of this dataset, including missing analytes, quality assurance parameters, and method information, PMF analysis revealed microbial dechlorination in the groundwater and provides insight about where dechlorination is occurring, to what extent, and under which geochemical conditions. PMF resolved a factor indicative of a source of 1,2,4-trichlorobenzene and 1,2-dichlorobenzene and two factors representing stages of dechlorination, one more advanced than the other. Factors were further interpreted using ancillary data such as geochemical indicators and field parameters also measured in the samples. Analysis suggested that the partial and advanced dechlorination signals occur under different environmental conditions. The results provided field validation of the current understanding of anaerobic dechlorination of chlorinated benzenes in the subsurface developed from laboratory studies. Partial dechlorination of trichlorobenzenes and

dichlorobenzenes appear to occur under lesser reducing conditions, such as sulfate-reducing conditions, whereas advanced dechlorination of monochlorobenzene to benzene and/or degradation of benzene may require highly reducing methanogenic conditions. PMF is thereby shown to be a useful tool for investigating chlorinated benzene dechlorination despite the heterogeneity of groundwater monitoring data.

2.1 Introduction

Chlorinated benzenes such as 1,2-dichlorobenzene and monochlorobenzene are used during the production of dyes, pesticides, disinfectants, and deodorants. Chlorinated benzenes are toxic to the kidneys, liver, thyroid and mucous membranes.[1] In addition, chlorinated benzenes can enter the human body via dermal contact, inhalation, ingestion, and eye contact and can bioconcentrate.[1] They were mainly used at the Chambers Works site as universal solvents in chemical processing. In 2008, the total annual release and transfer of 1,2-dichlorobenzene onsite was approximately 60,435 pounds.[2] According to the 2014 Environmental Protection Agency (EPA) Toxic Release Report (TRI) generated by the facility, chlorinated benzenes (1,2-dichlorobenzene and monochlorobenzene) were still being used onsite.[3] The Chambers Works facility historically used an open ditch system to dispose of waste such as spent solvents.[4, 5] The system did not have a liner and therefore allowed compounds to migrate into the subsurface and spread across the site via advection and diffusion in the groundwater. The environmental distribution at the former Chambers Works facility is a basis for concern due to the possibility of chronic exposure and its effects on human health. The compounds are found in over 140 wells at the site at levels exceeding the New Jersey

Department of Environmental Protection (NJ DEP) groundwater standards, which are
presented below in Section 2.3.1.

Chlorinated benzene concentrations have been measured in groundwater wells at the site
for over two decades (Figure 2-1). These compounds are the major contaminant of
concern, as they are widely detected in the sediment and groundwater across the site.
Chlorinated benzenes are found virtually everywhere in the B aquifer (Figure 2-2), where
their presence is attributed to onsite use. The B aquifer is a shallow aquifer system and
further information regarding the hydrogeology of the site is presented in Chapter 1. This
chemical transport between environmental compartments is governed by the physical-
chemical properties of the compounds and their interaction with other components in the
environmental system.

2.1.1 Properties of Chlorinated Benzenes

Despite their relatively high molecular weights and low vapor pressures, chlorinated
benzenes do evaporate from aqueous solutions, making them a more significant
environmental concern in the groundwater than in surface water and sediment.[1] There
are unique challenges associated with groundwater contamination with chlorinated
benzenes due to their densities being greater than that of water (i.e., 1.11 g/cm^3 for
monochlorobenzene).[6]   At Chambers Works, they are present in the groundwater in
both the aqueous phase and as Dense Non-aqueous Phase Liquids (DNAPLs). Upon
release, chlorinated benzenes can form pools and ganglia of DNAPL which sink to the
bottom of the aquifer and become lodged in cracks and fissures, persisting in the

subsurface for a considerable time.[6] DNAPL can serve as a source of down-gradient aqueous groundwater contamination as well as a sink for other contaminants in the subsurface, as organic contaminants can sorb and desorb in and out of the DNAPL phase to the aqueous phase.

2.1.2 Transport and Reaction Pathways of Chlorinated Benzenes

In addition to sorption, chlorinated benzenes will undergo transformation and mineralization reactions mediated by microorganisms also present in the subsurface, if provided favorable conditions. Groundwater contamination by chlorinated benzenes has been researched over the years.[7-25] Early studies identified microorganisms capable of mineralizing chlorinated benzenes via aerobic metabolic pathways.[20, 26] More recently, researchers have identified both aerobic and anaerobic dechlorination pathways by bacteria isolated from aquifer solids collected at this site.[16-18, 27-30] Enrichment cultures containing *Dehalobacter* spp. were shown to reductively dehalogenate all dichlorobenzene isomers to monochlorobenzene.[25] *Dehalobacter* spp. in sediment microcosms dehalogenated monochlorobenzene to benzene.[27] Recently, three *Dehalobacter* spp. showed varying chlorobenzene substrate specificity when enriched with different dichlorobenzenes (Figure 2-3).[28, 30] *Dehalobacter* strain 12DCB preferred singly flanked chlorines during reductive dechlorination and was capable of dechlorination to benzene.[30] Strain 13DCB was able to remove both singly and doubly flanked chlorines and strain 14DCB showed the narrowest substrate utilization range but dehalogenated para-substituted chlorines.[30] Coupling multiple strains of dehalogenating bacteria with a known benzene degrader has been shown to

achieve complete biodegradation via mineralization of benzene, which could be useful in cases where complete degradation does not occur or is too slow.[16] The favorability of anaerobic reductive chlorination of chlorinated benzenes generally increases with the degree of chlorination on the aromatic ring.[31] In contrast, the favorability of an oxidative attack decreases as the degree of chlorination increases.[31] Less chlorinated benzenes are therefore more amenable to aerobic degradation pathways.

2.1.3 Application of PMF to Chlorobenzene Groundwater Data

Recent studies at the site confirmed the presence of indigenous microbial communities capable of anaerobic reductive dechlorination of chlorinated benzenes [16-18, 27, 28, 30], implying that such dechlorination is occurring. However, such laboratory studies can only show what is *theoretically possible*. They do not demonstrate what is actually happening in the subsurface at Chambers Works. In this study, we analyzed the data for chlorobenzene concentrations in the subsurface, which should reveal what *is actually happening* or what happened a while ago up-gradient in the system. This data was analyzed using an advanced factor analysis tool called Positive Matrix Factorization (PMF).[32] PMF has been used to investigate the sources of atmospheric contaminants such as fine particulate matter[32-34], metals[35-43], volatile organics[44], and semivolatile organic compounds (SVOCs) such as PCBs.[45-59] PMF and other advanced factor analysis tools have been used to identify patterns of microbial dehalogenation of BDEs[59, 60], photochemical debromination of BDEs[59], and microbial dechlorination of PCBs[48, 49, 52-58] and PCDD/Fs[48-51, 58]. These

investigations were all performed using data from surface water, wastewater, and sediments.

It also should be noted that the various wells are screened at different depths (data not shown) and the screen intervals are often 5 to 10 feet (or greater) and they attempt to make sure the entire screening interval is within the target aquifer. As a result, the samples collected represent multiple stratigraphic layers, where redox conditions vary along with the consortia of microorganisms. During sample collection, the various redox conditions and niches of microorganisms are mixed together when the groundwater is mixed. Thus, these aqueous groundwater measurements may reflect different activities especially for different wells.

Application of PMF to groundwater data has been limited, although PMF was recently applied to groundwater data to apportion sources of PAHs in a karst aquifer.[61] PMF has not been widely used to analyze groundwater data because the conditions affecting groundwater contamination present certain complications in comparison to surface water systems. These include impeded air exchange with the atmosphere, laminar flow, and anaerobic conditions. Laminar flow coupled with anisotropy in the horizontal and vertical hydraulic connectivity and conductivity lead to limited mixing of chemical contaminants in the subsurface. Another issue arising from the nature of the contaminant class (chlorinated benzenes) in the subsurface is the *chromatographic effect* as they flow through the aquifer.[42] The *chromatographic effect* is a phenomenon in which organic contaminants separate from the contaminant plume.

In addition to these difficulties, which arise from the physical parameters of the system and the physico-chemical properties of the compounds of interest, there are other serious challenges associated with using PMF on the groundwater data from Chambers Works that are related to data collection and management. The data utilized here were collected for monitoring purposes, and are the type of data available for most contaminated sites. Other studies have collected data sets specifically for the purpose of detecting microbial dechlorination in the subsurface.[62] The purpose of this work was to determine whether dechlorination can be identified and understood using the data presently available, i.e. without expensive new data collection efforts. Challenges of this dataset include the application of different field sampling approaches as well as analytical methods where different sample preparation and instrumental techniques have been used throughout the years. In addition, method detection limits (MDLs) vary across samples and not all of the investigated analytes were measured in each sample, which could impact the cohesiveness of the dataset. Therefore the first aim of this work is to determine whether PMF can be successfully applied to groundwater monitoring data in order to investigate microbial dehalogenation in contaminated groundwater at the Chambers Works facility. If so, the second aim of this work is to utilize an innovative data mining approach to provide additional evidence of the occurrence of microbial dechlorination as well as insights as to when, where, and under which conditions it takes place. We know dechlorination is occurring in the subsurface at the site [28, 30] and therefore we are further examining it using this intimate data mining approach. Furthermore, the PMF model provides information as to how much mass of a compound is attributed to

dechlorination versus another source (such as use onsite). Thus the PMF approach should in theory allow us to provide not only evidence of dechlorination, but also an estimate of the extent of the dechlorination that has already occurred. This supplementary evidence of *in situ* dechlorination processes may help alleviate the burdens of compliance with state regulators.

2.1.4 Goals of This Work

Thus the goals of this work are to: a) determine whether the chlorinated benzene data can be successfully analyzed by PMF; b) determine whether PMF can give useful information of microbial degradation processes in groundwater; c) if so, to investigate where and when microbial dechlorination of chlorinated benzenes has occurred in the subsurface at Chambers Works; and d) investigate correlations between PMF outputs related to microbial degradation and ancillary parameters such as redox indicators, alkalinity and nutrients in order to understand which conditions favor microbial degradation.

2.2 Methods

2.2.1 Site Description

The Chamber Works facility was owned and operated by the DuPont Corporation from 1917 to 2015, when it was spun off as The Chemours Company. It is located in Deepwater, New Jersey and covers approximately 1,455 acres. The site suffers from a variety of environmental problems including groundwater pollution by chlorinated benzenes. There is an onsite water resource recovery facility (43 MGD), which supports various chemical-manufacturing processes in addition to groundwater recovery programs.

There are three groundwater recovery programs operating onsite and six active

monitoring programs.[4] A total of 96 active monitoring wells throughout 16 unique

areas of concern are routinely sampled for various VOCs, SVOCs, and heavy metals

groundwater contaminants as well as ancillary field parameters such as temperature,

dissolved oxygen, pH, nutrients, and redox indicators.[4] Further information regarding

the site and the groundwater monitoring program can be found in Chapter 1.

2.2.2 Analytes in PMF Analysis

A wide variety of groundwater contaminants have been measured onsite. In this study,

we focused on the chlorinated benzenes. The measured compounds of interest include

1,2,4-trichlorobenzene (1,2,4-TCB), 1,4-dichlorobenzene (1,4-DCB), 1,3-

dichlorobenzene (1,3-DCB), 1,2-dichlorobenzene (1,2-DCB), monochlorobenzene (CB),

and benzene (Table 2-1). Other chlorinated benzenes including hexachlorobenzene,

pentachlorobenzene, 1,2,4,5-tetrachlorobenzene and 1,2,3-trichlorobenzene are present in

the database, however these analytes are below the limit of detection in more than 50% of

the entire dataset and thus excluded from the PMF analysis due to the lack of data.

Measurements of each compound taken as early as 1990 are present in the database.

Various analytical methods were used to measure the chlorinated benzenes in aqueous

phase groundwater and solid phase samples throughout the 1990s.

PMF analysis requires an estimate of uncertainty in the measured concentrations. During

sample collection and processing, there is the potential for analyte mass to be lost. For

SVOC and VOC compounds, such as chlorinated benzenes and benzene, mass can be lost

due to their volatilization. Loss of analyte mass in both solid and aqueous phase samples can occur in the field during sample collection, transport, storage and processing. Sample preparation for SVOCs and VOCs in environmental matrices generally involves analyte extraction and measurement via chromatography. Some methods may require additional preparation steps including sample cleanup to remove matrix interferences, as well as organic solvent volume reduction or solvent exchange of the sample extract before instrumental analysis. In order to quantify analyte losses that may occur during these many steps, quality control procedures may require the use of field surrogates and field sample duplicates to assess matrix effects between the time of sample collection and laboratory preparation. Field surrogates are used to quantify analyte loss (% mass recovery) between sample collections through analysis. Field duplicates indicate the reproducibly of the sample collection and processing. Analytical quality control procedures also include the use of laboratory duplicates and surrogates as well as cleanup surrogates and laboratory control samples (LCS) in order to document matrix effects on method performance. Laboratory duplicates provide information regarding the reproducibility of a set of data from a given sample matrix. The % mass recovery of target analytes is determined through the use of surrogates that are either added to the sample matrix (laboratory and cleanup surrogates) or reagent blanks (LCS).

With the exception of a few samples collected in 1993, EPA method 8270 series (A, B, and C) were used to measure tri- and dichlorinated benzenes (1,2,4-TCB, 1,4-DCB, 1,3-DCB, and 1,2-DCB) and the method 8240 series (A, B, and C) were used to measure CB and benzene. Details of these methods are as follows.

1990-1994: EPA method 8270 was used for chlorinated benzenes, 1,2,4-TCB, 1,4-DCB, 1,3-DCB, and 1,2-DCB in the early 1990s, however both CB and benzene were determined by EPA method 8240. EPA method 8270 outlines the analysis of SVOCs in air, water, soil, biota, and various solid waste matrices by gas chromatography/mass spectrometry (GC/MS). Method 8270 requires the use of laboratory surrogate spike recovery standards to assess percent mass loss during sample preparation and uses the internal standard method of quantification. The following laboratory surrogate standards are used in method 8270: phenol-d_6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d_5, 2-fluorobiphenyl, and p-terphenyl-d_{14}. The following internal standards are used: 1,4-dichlorobenzene-d_4, napthalene-d_8, acenapthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}. In addition, EPA method 8240 is used to determine volatile organic compounds (VOCs) by GC/MS for various solid waste matrices as well as aqueous samples including groundwater. Method 8240 also incorporates the use of surrogate and internals standards. The laboratory surrogate standards for method 8240 are 4-bromofluorobenzene, 1,2-dichloroethane-d_4, and toluene-d_8 and internal standards are bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d_5.

1994: Method 8270A was used to measure 1,2,4-TCB and DCBs and method 8240A was used to measure CB and benzene.

1995-1998: Method 8270B was used for 1,2,4-TCB and DCBs and method 8240B was used for CB and benzene, respectively.

August 1998-2011: Method 8270C was used to measure 1,2,4-TCB and DCBs and method 8260B was used to measure CB and benzene. EPA method 8260 also describes the analysis of VOCs by GC/MS and the transition from 8240 is attributed to the use of a capillary chromatographic column in 8260. Method 8260 uses internal and surrogate standards. The recommended surrogate standards are toluene-d_8, 4-bromofluorobenzene, 1,2-dichloroethane-d_4, and dibromofluoromethane and the recommended internal standards are fluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4. The revisions of method 8270 (e.g., 8270A, 8270B, 8270C, and 8270D) are due to the difficulty of simultaneous measurement of acid, base, and neutral organic compounds (over 70 compounds) over a wide concentration range.

Exceptions: For 22 samples collected in 1993, EPA method 625 was used to measure 1,2,4-TCB and DCB isomers, whereas EPA method 624 was used to measure CB and benzene. Method 624 is used to analyze purgeable VOCs, which are prepared by a purge and trap method and uses surrogate standards and internal standards. The following compounds can be used as either surrogate or internal standards for method 624: pentafluorobenzene, fluorobenzene, 1-bromo-4-fluorobenzene, bromochloromethane, 2-bromo-1-chloropropane, 1,4-dichlorobutane, benzene-d_6, 1,4-dichloroethane-d_4, ethylenzene-d_5, ethylbenzene-d_{10}. Method 624 uses field reagent blanks and field duplicates. Method 625 outlines the determination of acid, base and neutral SVOCs by GC/MS. Method 625 use internal and surrogate standards and suggest collecting field duplicates. Method 625 internal and surrogate standards include aniline-d_5, anthracene-

d_{10}, benzo(a)anthracene-d_{12}, 4-4'-dibromobiphenyl, 4,4'-dibromooctafluorobiphenyl, decafluorobiphenyl, 2,2'difluorobiphenyl, 4-fluoroaniline, 1-fluoronapthalene, 2-fluoronapthalene, napthalene-d_8, nitrobenzene-d_5, 2,3,4,5,6,-pentafluorobiphenyl, phenathrene-d_{10}, pyridine-d_5, 2-fluorophenol, pentafluorohenol, phenol-d_5, and 2-perfluoromethyl phenol.

Although the abovementioned analytical methods require the use of surrogate and internal standards, it should be noted that no data regarding these parameters were available in the database. In addition, none of these methods suggest the use of field surrogates. Useful information for factor analysis includes laboratory surrogate recoveries and field surrogate recoveries are also highly desirable. Because methods often substitute standards and certain methods provide choices of standards (e.g., Method 624 and 625), it would be helpful to know which standards used for each measurement. Lastly, various laboratories have measured samples collected from the site over the past two decades. In the 1990s, ETC, Ponca City, and Enseco-East and Lancaster laboratories analyzed the groundwater samples. As of the late 1990s, Lancaster Laboratories primarily analyzed groundwater samples.

2.2.3 Ancillary Parameters

Ancillary parameters investigated here include temperature (T, n = 401 of 597 samples), pH (n = 470), redox (pE, n = 320), dissolved oxygen (DO, n = 396), alkalinity (ALK, n = 144), total organic carbon (TOC, n = 500), total dissolved solids (TDS, n = 401), nitrate (NO_3^-, n = 33), nitrite (NO_2^-, n = 74), sulfate (SO_4^{2-}, n = 191), sulfide (S^{2-}, n = 67),

methane (CH_4, n = 127), total ferric iron (Fe^{3+}, n = 63), total ferrous iron (Fe^{2+}, n = 71).

Analytical methods by which these ancillary parameters were measured are reported in

Chapter 1. Ancillary parameters were used to understand and correlate the PMF results,

but these were not always measured in the 597 samples used in the PMF analysis of the

chlorobenzene data. The majority of the parameters can be used as indicators of the

redox environment in the subsurface. Some of these ancillary measurements are subject

to error due to their inherit transience (i.e., ferric iron and methane). Even seemingly

straightforward field measurements such as pH and DO can be confounded if the proper

sampling technique is not used (low-flow technique) and if the handheld probes are not

sufficiently calibrated during the lifespan.[63] In addition, the integrity of the sample

may be sacrificed if samples are not handled carefully and measured immediately.

In addition to these data quality issues, there are data quantity issues as well. In many

cases, insufficient samples were available in which both the CBs and the ancillary

parameters were measured (e.g., phosphate, n = 21 and bicarbonate n = 16). In order to

avoid some of these problems, we developed an additional 'ancillary' metric based on

compounds routinely measured along with the chlorobenzenes, viz., the fraction of

aniline as the sum of aniline and nitrobenzene (%AN) as a redox measurement. The fact

that nitrobenzene and aniline were measured using similar methods to the CBs in the

same samples should allow many of the matrix effects to cancel out. Statistical

significance tests and p-values calculated between this parameter and other ancillary

measurements demonstrate that %AN is an independent redox measurement, as it does

not correlate with any other ancillary measurement. Additionally, aniline and

nitrobenzene were measured along with chlorinated benzenes in the same sample, providing a large number of data points for the correlations (n = 418 out of the 497 total samples), and potentially negating some problems associated with sample matrix effects. Although use of %AN as a redox indicator overcomes some of the problems associated with the other redox indicators, it should be noted that %AN has problems of its own. In particular, laboratory measurements of aniline can be problematic due to its tendency to undergo electrostatic interactions.[64]

2.2.4 PMF Input Data Matrices

Groundwater data regarding chlorinated benzenes measured in aquifers A, B, C, D, and E was retrieved from the Envista database developed by DuPont/Chemours. The sample dates range from January 9, 1990 to September 9, 2011. A total of 1,552 groundwater water samples, in which hexachlorobenzene, pentachlorobenzene, 1,2,4,5-tetrachlorobenzene, 1,2,3,4-tetrachlorobenzene, 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, monochlorobenzene and benzene were measured, were retrieved. In more than 50% of these samples, no chlorobenzenes or benzene were detected; of course these samples could not be used for the PMF modeling. Hexachlorobenzene, pentachlorobenzene, 1,2,4,5-tetrachlorobenzene, 1,2,3,4-tetrachlorobenzene, and 1,2,3-trichlorobenzene were below detection limit (BDL) in more than half of the remaining samples, and so were not included in subsequent PMF modeling. This resulted in a final dataset consisting of 6 analytes (Table 2-1) and 597 samples with only 12% of the measurements BDL. As a

result, aqueous phase groundwater concentration data ($X_{i,j}$) for 3,582 data points were submitted to PMF 2.0 software (YP-Tekniika KY Co., Helsinki, Finland).

For PMF2 analysis, three matrixes are submitted to the program: concentration, limits of detection (LOD), and uncertainty matrixes. For the concentration matrix, BDL values were replaced with a random number between zero and the method detection limit (MDL). There were no non-measured ('missing') values in the concentration matrix. The LOD matrix was assembled with the reported MDLs for each data point. For the uncertainty matrix, a (x, 3x) matrix was used[48, 54, 55, 57, 59, 65-67], where x is the uncertainty assigned to all detected measurements and three times this value (3x) is assigned to all those measurements BDL. The calculated relative standard deviation (RSD) of the surrogate recoveries is frequently used as x.[54, 67] However, surrogate recoveries for each measurement were not available. As stated above, multiple analytical methods were used to analyze the investigated chlorinated benzenes and benzene in the samples included in the analysis. Although quality control laboratory surrogate are reported in the analytical methods, data regarding the % mass recovery of the standard in each sample was very limited. Only data between 2008-2011 provided surrogate recoveries for the one surrogate (1,4-dichlorobenzene-d_4) that was used for all six analytes. Furthermore, field surrogates, which could have provided substantial information regarding error introduced during field sampling, were not used.

In our experience with PMF2, the solution becomes unstable (or less stable) when the uncertainty matrix gives the same uncertainty for all analytes. The uncertainty (x) should be unique for each analyte, or at least those analytes with similar physical-chemical

properties (or the same degree of halogenation on the aromatic ring). Those

measurements BDL should be assigned a higher uncertainty (3x) in comparison to those

detected measurements, which are given a lower uncertainty assignment (x). Since

suitable surrogate recoveries data were not available, we assigned an uncertainty value to

each compound using our best judgment after reviewing the available information

regarding the analytical method and after considering each compound's physical-

chemical properties and their implications during field sampling activities. Benzene and

CB were assigned an uncertainty value of 0.15 (dimensionless) for all those detected

measurements. 1,2,4-TCB, 1,3-DCB, and 1,4-DCB were assigned an uncertainty of 0.13,

whereas 0.1 was assigned to all those detected measurements of 1,2-DCB. Again, all

measurements BDL were assigned three times the aforementioned values for each

respective analyte. We decided to assign a higher uncertainty to CB and benzene due to

these compounds' volatility and reactivity in the subsurface. 1,2-DCB was assigned the

lowest uncertainty because it is often present in the highest concentrations usually well

above the MDL. There is not a large range between these uncertainty assignments and,

for the most part, more volatile and/or reactive compounds are assigned a slightly higher

uncertainty (i.e., $x = 0.15$ for benzene, versus $x = 0.1$ for 1,2-DCB).

2.2.5 Spatial Trends

The ArcGIS software (version 10.2.2) enabled us to map model solutions in the wells

throughout the dates considered in the study (Figure 2-1).

2.2.6 Correlation Analysis

Spearman's rank-order correlation of the strength of each factor in each sample (i.e., G-matrix aka mass contribution) was used to examine correlations with measurements of ancillary parameters such as pH, redox indicators, and nutrients to identify locations where microbial dechlorination is occurring in the subsurface. For these correlations, the samples were ranked two ways: first by the absolute concentration of each factor, and second by the relative contribution of each factor to each sample (i.e. the factor concentration in a given sample was divided by the sum of all of the factors for that sample and this percentage was ranked). In addition, Spearman's rank-order correlations were performed in attempt to identify trends between ancillary measurements and the raw analyte concentrations (i.e. prior to PMF analysis). Correlations were performed on the ranked absolute measured concentration (ppb) data after preprocessing for PMF analysis as well as on *normalized* (i.e. percent of total) concentration data.

Spearman's correlation coefficient is defined as the Pearson's correlation coefficient between two ranked variables. Spearman's correlation is a non-parametric statistical analysis, and has been applied to assess monitoring data such as surface water[68] and groundwater[62, 69, 70] quality data. The method is well suited to the analysis because it makes no assumptions about the distribution of the data and is more appropriate for datasets with large outliers that mask meaningful relationships.

2.3 Results

2.3.1 Description of Dataset

The 10th, 50th, and 90th percentile concentrations of the CBs as well as the ancillary parameters are reported in Table 2-2. The concentrations presented were performed on the same data set used for PMF analysis (i.e. BDL data replaced by a random number between zero and the MDL). CB concentrations are highest in the southern portion of Chambers Works but these compounds are ubiquitous throughout the facility. The NJ Class IIA groundwater quality criteria for 1,2,4-TCB, 1,2-DCB, 1,3-DCB, 1,4-DCB, CB, and benzene are 9 µg/L, 600 µg/L, 600 µg/L, 75 µg/L, 50 µg/L, and 0.2 µg/L, respectively. Concentrations of 1,2,4-TCB, 1,2-DCB, 1,3-DCB, 1,4-DCB, CB, and benzene range from 1 to 630,000 µg/L, 1 to 230,000 µg/L, 0.6 to 2,300 µg/L, 0.6 to 49,000 µg/L, 1 to 78,000 µg/L, 0.5 to 51,000 µg/L, respectively.

2.3.2 Correlations with Absolute Analyte Concentration Data

Spearman correlations were performed on the ranked absolute measured concentration (ppb) data after preprocessing for PMF analysis as well as on *normalized* concentration data (Table 2-3). The results were compared with similar correlations between ancillary measurements and the PMF results to determine whether PMF analysis contributed to a better understanding of the data than careful examination alone.

The following bulleted list compares the results from correlation analysis of ancillary measurements including geochemical data and redox indicators versus absolute concentrations of the investigated analytes and the percent of total mass of each analyte

(*relative* concentrations). Elevated concentrations of the investigated CB analytes and ancillary parameters, such as sulfate and TOC (Table 2-2), were applied to the correlation analysis contributing too many positive relationships. In this case, correlations using only absolute concentrations may be misleading and correlations using *relative* concentrations reveal relationships that would be otherwise unnoticed.

2.3.2.1 Geochemical Data & Redox Indicators

- Nitrate: Nitrate showed no relationships with absolute or *relative* concentrations of the investigated analytes.

- Nitrite: For absolute concentrations, nitrite was positively correlated with benzene. For relative concentrations, nitrite was positively correlated with benzene, but negatively correlated with 1,3-DCB and 1,4-DCB. Dechlorination of CB to benzene or the degradation of benzene may occur under lesser reducing (slightly oxidizing) conditions onsite, which are typical of nitrate reduction.[19, 24, 71] Also, dechlorination of trichlorobenzenes might be inhibited by the presence of nitrite.

- Ferric iron: Correlations using absolute concentration of analytes show no significant relationships, however the results using *relative* concentrations of analytes show a negative relationship with 1,2-DCB.

- Ferrous iron: For both absolute and relative concentrations, ferrous iron is negatively correlated with 1,2,4-TCB and 1,3-DCB. In addition, relative concentrations of ferrous iron are positively correlated with benzene. It should be

noted, Spearman correlation between ferric and ferrous groundwater concentrations reveals a positive correlation ($p = 0.007$, $n = 31$).

- Sulfate: Results of correlations between sulfate and absolute concentrations of the analytes display a positive correlation for all investigated analytes (1,2,4-TCB, 1,2-DCB, 1,3-DCB, 1,4-DCB, CB, and benzene). Results of correlations between sulfate and *relative* concentrations of the analytes show the same positive relationship only for 1,2-DCB and negative relationships with 1,4-DCB and CB.

- Sulfide: Results of correlations between sulfide and absolute concentrations of the analytes show a positive correlation between sulfide and 1,4-DCB. In contrast, correlations results with *relative* concentrations of the analytes and sulfide show a negative relationship with benzene. Dechlorination of chlorinated benzenes could be occurring under sulfate-reducing conditions.[72]

- Methane: For absolute concentrations, methane is positively correlated with 1,2-DCB, 1,4-DCB, CB, and benzene. For *relative* concentrations, methane is negatively correlated with 1,2,4-TCB, 1,3-DCB, and 1,4-DCB and positively correlated with benzene. Reductive dechlorination of chlorinated benzenes is generally observed under methanogenic conditions.[28, 30, 72, 73]

- Redox, Eh (field): No relationships were revealed from correlations between oxidation-reduction potential (redox, Eh) and the absolute concentrations of the investigated analytes. Correlation results using *relative* concentrations of the analytes and redox reveal a negative relationship with 1,3-DCB. These results make sense since anaerobic reductive dechlorination requires a reducing environment (oxidation-reduction potential < -100 mV).[74]

- %AN: For absolute concentrations, %AN is positively correlated with 1,4-DCB, CB, and benzene. For *relative* concentration, %AN is positively correlated with only CB and benzene, and negatively correlated with 1,2,4-TCB, 1,2-DCB, and 1,3-DCB. This suggests that analytes emitted to the groundwater (such as 1,2,4-TCB and 1,2-DCB) are present in more oxidizing (less reducing) conditions, whereas prospective dechlorination products such as CB and benzene are present in more reducing (less oxidizing) environments. The discrepancy between the negative correlation between 1,3-DCB and %AN with the negative correlation between 1,3-DCB and pE might be attributed to inhibition [75, 76] in the presence of aniline or where there are elevated concentrations of aniline due to its toxicity.

2.3.2.2 Nutrients & Field Parameters

- TOC: For absolute concentrations, TOC is positively correlated with all investigated analytes (1,2,4-TCB, 1,2-DCB, 1,3-DCB, 1,4-DCB, CB, and benzene). For relative concentrations, TOC is again positively correlated with benzene, but *negatively* correlated with 1,2,4-TCB, 1,3-DCB, and 1,4-DCB. A sorption effect could explain the negative relationship between 1,2,4-TCB, 1,3-DCB, 1,4-DCB and TOC. Less sorption may take place where there is less TOC available to sorb onto/into, assuming TOC is a good indicator of bioavailable organic matter. Since sulfate reduction and dechlorination will more readily occur when there is enough bioavailable organic carbon in the system, the negative correlations with relative concentrations of tri- and di- chlorinated benzenes and TOC may indicate that these compounds are being degraded under

sulfate-reducing conditions.[31] Sulfate and TOC (after preprocessing for PMF

analysis) are not correlated with each other (p = 0. 50, n = 72), but sulfide and

TOC are positively correlated (p = 0.007, n = 35), and TDS and TOC are strongly

correlated (n = 137, p = 10^{-9}).

- Alkalinity: For absolute concentrations, alkalinity is positively correlated with

  benzene and CB. For relative concentrations, alkalinity is again positively

  correlated with benzene, but negatively correlated with 1,2,4-TCB and not

  correlated with CB. Since alkalinity is considered an indicator of anaerobic

  microbial activity[77], its correlation with CB and benzene suggests that they are

  products of microbial degradation. This is in agreement with the current

  understanding of the pathways of CB degradation reviewed above.

- pH (field): For absolute concentrations, pH is negatively correlated with 1,2-

  DCB, 1,4-DCB, CB, and benzene. For relative concentrations, pH is only

  negatively correlated with 1,2-DCB, and is instead positively correlated with

  1,2,4-TCB, 1,3-DCB, and 1,4-DCB. The discrepancy between the alkalinity and

  pH correlations with 1,2,4-TCB may be associated with a buffer effect. Here,

  alkalinity was measured as total carbonate alkalinity. Lastly, 1,2-DCB is known

  to be the main contaminant emitted directly to the groundwater and is often

  present in the form of DNAPL (pure liquid phase). An environment where the pH

  < 5.5 may inhibit dechlorinators.[74] It should be noted that some anaerobic

  microbial processes, including nitrate-, iron- and sulfate reduction, generate

  alkalinity / consume hydrogen ions (H^+).[31] The absence of one or more of these

  processes may inadvertently contribute to acidification of the subsurface

environment. Furthermore, fermentation, which is also an anaerobic process, produces H_2 and can also cause acidification in groundwater.[74]

- Temperature (field): For absolute concentrations, temperature is negatively correlated with benzene. For relative concentrations, temperature is again negatively correlated with benzene, and is positively correlated with 1,2,4-TCB, 1,3-DCB and 1,4-DCB. The aqueous solubility of trichlorobenzenes and dichlorobenzenes increases with increasing temperature (assuming no increases in salinity).[6] It is surprising to see the positive correlation between 1,2,4-TCB and temperature given the oxidizing conditions suggested by results from other ancillary correlation such as %AN and ferrous iron. Oxygen, amongst other gases, is generally more soluble in aqueous solution at lower temperatures.[6] Microbial activity generally increases with increasing temperature[31], which could explain the positive correlation between temperature and parent compounds (tri- and di-CBs) and the negative correlation with the CB-dechlorination end product (benzene). An alternate explanation for the negative relationship between benzene and temperature is volatilization. At higher temperatures, benzene, the most volatile of the analytes, will more readily volatilize out of aqueous solution during sample collection.

2.3.3 PMF Analysis

The PMF model was run requesting 2 to 6 factors starting at 10 different initialization points (seed values) for each requested number of factors. The 3-factor solution was

determined to be the 'correct' number of factors for this dataset for the following six reasons outlined below.

- First, to ensure that all factors contributed positively and significantly to the measured sum of the analytes, the three factor G-matrix (the mass contribution of each factor to a given sample) was regressed against the sum of the analytes, and all gave positive and significant ($p < 0.05$) coefficients. This multiple linear regression (MLR) indicates when factors have been generated that do not contribute positively and significantly to the overall solution, i.e. too many factors have been requested.

- Second, the model results are stable and reproducible. The relative standard deviation (RSD) of the G and F matrixes (the F matrix describes the chemical profiles or *fingerprints*) always display a similar level of reproducibility and are commonly used an indicator of model stability.[54, 55, 58, 67] Here we chose the highest number of factors that provide a stable model solution, i.e. three (Table 2-4). The average RSD of the G and F matrixes for all 10 seed runs in the three-factor model were quite low (0.6% and 4.3%, respectively), demonstrating that the quality of the data is sufficient that PMF analysis can be performed and can yield stable model solutions, which addresses the first objective, goal A, mentioned above.

- Third, the resolved factors are independent. G-space plots were examined to ensure that all source contributions are independent of each other. The plots are graphs of the G-matrix of one factor versus the G-matrix of another factor and can be used to assess rotational ambiguity. Additionally, the plots provide

information regarding the relationship between source contributions. G-space plots indicate each factor is independent of the others and rotation of the data matrix is not necessary (Figure 2-4).

- Fourth, plots of modeled versus measured concentrations are in good agreement. The chosen number of factors must provide a good fit (correlation) between the measured concentrations and the modeled analyte concentrations. The overall agreement between the measured and modeled concentrations increase in comparison to the 2-factor model. The 3-factor model yielded an R^2 value better than 0.65 for the six analytes, two of which are greater than 0.90 (for 1,2-DCB and benzene).

- The fifth criterion for determining the correct number of factors is that the model results have physical meaning. The fact that PMF resolved factors resembling stages of dechlorination is a good indicator of this. In addition, too many factors should not be requested for this data matrix because the dataset is relatively small and contains few analytes. For example, it would not make sense to accept a 6-factor solution when there are only 6 analytes included in the model.

- The sixth and final criterion for determining the correct number of factors is that results from analyzing variations of the input matrices with PMF are in agreement with those presented. This sensitivity analysis is presented in the section below.

2.3.4 Sensitivity Analysis of Input Matrices

A sensitivity analysis was performed in an effort to understand the importance of the uncertainty and limit of detection matrices. Various permutations of the data matrices

were applied to the model in order to understand the best way to apply the PMF2 model to this particular monitoring dataset. The base uncertainty was increased and decreased (i.e. the base uncertainty, x, was multiplied by $10, 2, 0.5,$ and 0.1). In other runs, a random value was assigned to the base uncertainty (x), while keeping the limit of detection (LOD) and concentration matrices constant using base case (original) values. Permutations were applied to the LOD matrix in a similar manner except that the other matrices were adjusted relative to the applied permutations, i.e. when an LOD was increased to a value higher than the measured concentration, the uncertainty was increased to 3x. In addition, those measurements BDL were assigned a random value between 0 and the newly assigned, artificial, MDL in the concentration matrix. A consensus 3-factor solution was found by running the PMF2 model on the variations of the LOD and uncertainty matrices. Regardless of how the detection limit and uncertainty matrices were assembled, the model still resolved 3-factors similar to the final solution presented below. Although different strengths of these factors were resolved (i.e. small changes in the G matrix), the solution was consistent and stable indicating that the 3-factor solution best describes the groundwater monitoring dataset. Three source profiles resolved always included a source term (1,2-DCB), a partial degradation term (CB), and an advanced degradation term (CB and benzene).

2.3.5 Chlorinated Benzene Source Profiles

The PMF model resolved three source profiles (factors) in the groundwater monitoring dataset of the chlorinated benzenes (Figure 2-5). Factor 1 is comprised of virtually all 1,2-DCB and constitutes 43% of the total mass of all analytes in the dataset. Factor 1

also contains nearly all of the mass of 1,2,4-TCB in the dataset. Based on the historic

use of 1,2-DCB onsite we conclude factor 1 is a source term.

Factor 2 is comprised of 91% CB, 7.5% 1,4-DCB, and 1.5% 1,3-DCB and constitutes

44% of the total mass of all analytes in the dataset. Factor 2 contains virtually all of the

mass of 1,3-DCB, 1,4-DCB, and CB. Since factor 2 contains virtually all of the mass of

both 1,3- and 1,4-DCB, factor 2 may represent partial dechlorination of polychlorinated

benzenes to dichlorobenzene isomers and CB. While 1,2,4-TCB can be dechlorinated to

all three DCB isomers, laboratory studies have shown 1,4-DCB is typically the most

favored product of 1,2,4-TCB dechlorination.[17, 73, 75]

Factor 3 consists of ~1:3 ratio of CB and benzene and contains virtually all of the

benzene in the dataset. Factor 3 consists of 13% of the total mass of the solution. Factor

3 is believed to represent an advanced stage of dechlorination of monochlorobenzene to

benzene and/or degradation of benzene.

It is helpful to consider the octanol-water partition coefficient (K_{ow}) and the Henry's law

constant (K_H) of each analyte (Table 2-2) in order to determine whether the factors are

indicative of physical processes. K_{ow} is an indicator of the hydrophobicity of a chemical

compound and K_H is an indicator of the volatility of a compound from aqueous

solution.[78] The K_H values provides insight to how readily a chemical compound would

volatilize out of the aqueous phase and into air. The K_{ow} values reveal how readily the

compound would partition out of aqueous and onto organic material such as aquifer

solids, biomass, or even DNAPL.

If the concentrations of the analytes were primarily controlled by physico-chemical

properties and the chromatographic effect, 1,2-DCB would be found in the same factor as

1,3-DCB due to their similar K_{ow} and K_H values. Similarly, 1,4-DCB would not be in the

same factor as 1,2,4-TCB because they have very different K_{ow} values. Furthermore, CB

and benzene would not be found in the same factor because they have very different K_H

values. The PMF results therefore suggest that the CB fingerprints are not a product of

the physico-chemical properties of the analytes. Note also that the PMF model does not

isolate a factor with nothing but benzene. Such a factor would have suggested that there

was a primary source of benzene onsite. The lack of one suggests that virtually all of the

benzene is associated with CB, and therefore that virtually all of the benzene arises from

dechlorination of chlorobenzenes.

The fact these patterns are observed and the PMF results are interpretable and tell a

coherent story about the fate of CBs in the subsurface suggests that PMF is a useful tool

for analyzing groundwater data. These results address the second objective, goal B, of

the work.

2.3.6 Temporal and Spatial Trends in PMF Factors

A total of 191 wells had enough data to assess spatial trends of the concentrations of the

mass contribution (G-matrix) of each factor in the chlorinated benzene PMF solution

(Figure 2-1). In Figure 2-6 the absolute concentration of each factor is displayed throughout the investigated years of the study between January 1990 and September 2011. The percent of the total mass contribution (*relative* concentrations of the G-matrix) of each factor in each well is displayed throughout the study period in Figure 2-7. Many 'hot spots' of the advanced degradation (factor 3) appear to be located on the perimeter of the site, whereas only a few appear in the center of the site. The fact that many 'hot spots' of the advanced degradation factor appear at the perimeter of the site makes sense if the degradation products are traveling away from source zones. In addition, there could be something that is required for degradation but is depleted in the source zone such as sulfate. 'Hot spots' of the source term (factor 1) and the partial degradation factor (factor 2) are spread out across the site, with grouping occurring near the perimeter and the canal area. All three factors occur in different places from each other, suggesting the two reductive dechlorination regimes occur under different conditions.

Wells with more than 10 sampling events were examined individually. The time and spatial trends of the factors suggest that dechlorination conditions differ not only by well location but also by time within locations, which addresses the third objective (goal C) of the work. Some wells do not achieve the advanced CB-dechlorination regime and the partial dechlorination regime is only observed. Different microorganisms may mediate the partial and advanced CB- dechlorination regimes. Microbial growth and activity is impacted by temperature, pH, substrate, as well as the bioavailability of nutrients and electron acceptors in the subsurface.[31] Observations about some of these wells are described below.

- Monitoring well C07-M01B is a B aquifer well located in the southwestern corner of the site adjacent to the Delaware River and Salem Canal. The samples included in the study (n = 13) for C07-M01B were collected between June 1990 and July 2011 (Figure 2-8). The partial dechlorination regime appears to be occurring in C07-M01B, however, the advanced dechlorination regime is not. Alkalinity, methane, ferric iron, ferrous iron and sulfide aqueous concentration data are either below detection limit or not measured with the investigated analytes in the preprocessed PMF dataset for this well. The aforementioned data are either non-detected or not measured with the investigated analytes in the preprocessed PMF dataset. There are few measurements for sulfate (110,100 μ g/L, June 1990; 66,200 μ g/L, May 1993), nitrate (500 μ g/L, June 1990; 200 μ g/L, May 1991) and nitrite (400 μ g/L, May 1994). %AN values are 87% and 92% from measurements taken in May 1991 and May 1994, respectively, suggesting reducing conditions in this well. In addition, pH measurements were taken between 1990 and 2011 and range between 6.8 (in 2001) to 10.5 (in 1990) with an average pH (n = 11) value of 7.9. Temperature values between 1994 and 2011 range from 14.4C (in 1994) to 23.7C (in 1998) with an average temperature (n = 9) of 19.0C. There is not enough supplementary data available to deduce the redox environment throughout the observation period, although the presence of nitrate and the %AN results suggest it is at least mildly reducing. Physical conditions such and pH and temperature appear to be in a favorable range to sustain reductive dechlorination.[74] Low total concentration of the dechlorination intermediate compound, CB, may explain why the advanced

dechlorination regime appears to not be active in C07-M01B. The average CB concentration in well C07-M01B between 1990 and 2011 is 50 µg/L (n = 13) with a minimum concentration of 7 µg/L (in 1998), a maximum concentration of 156 µg/L (in 1993), and the 50th percentile concentration is 31 µg/L. The threshold to continue CB-dechlorination might be higher than that to start it.[28, 30]

- Mass recovery well K06-R02C/D penetrates the deeper C and D aquifers. This well is also located on the southern portion of the site adjacent to the Salem Canal. Eleven samples were collected between April 1994 and July 2011 (Figure 2-9). The partial dechlorination factor increased in this well after 2001, whereas the advanced dechlorination factor does not appear at all. There is no available data regarding aqueous groundwater concentrations of alkalinity, nitrate, nitrite, ferric iron, ferrous iron, sulfate, sulfide or methane in K06-R02C/D. %AN data are available (n = 11) between April 1994 to July 2011 and range between 14% (in 1998 and 200) to 41% (in 2011) with an average of 22%suggesting a lesser-reducing (more oxidizing) environment. Also, pH measurements between April 1994 and July 2011 and range from 5.7 (in 1996) to 6.6 (in 1997) with an average pH of 6.2 (n = 11), i.e. a slightly acidic environment. Few temperature measurements are available from the 1990s (T = 17.6C in April 1994, T = 13.9C in 1996; and T = 18.1C in July 1997). The appearance of dechlorination products in this well after 2001 may suggest that the subsurface environment became more favorable for the dechlorinating bacteria to mediate the partial CB-dechlorination regime over time or that bacteria adapted to the physical environment to mediate the reductive dechlorination process under provided conditions. Alternatively,

and perhaps most likely given the relatively unfavorable conditions in this well as
well as its depth, dechlorination products may have been transported here from
elsewhere on the site.

- Monitoring well G05-M02B penetrates the B aquifer on the southern portion of
  the site adjacent to the Salem Canal. These samples (n = 16) were collected
  between April 1994 and July 2011 (Figure 2-10). In this well, both the partial and
  advanced dechlorination factors follow similar time trends, which suggest either
  both factors come from the same source or they both are being transported
  together in the subsurface. Concentrations of ferric iron, ferrous iron, nitrate, and
  sulfide are not available for G05-M02B and few measurements of sulfate
  (140,000 μg/L in August 1994 and 92,700 μg/L in July 1990), methane (6,300 μ
  g/L in July 2009), and alkalinity (81,900 μg/L in July 2009). %AN
  measurements are available (n = 14) between August 1998 and July 2011 and
  range from 55% (in 1998) to 100% (in 2009) with an average %An value of 89%.
  The pH measurements between August 1998 and July 2009 indicate a slightly
  acidic environment and values range from 5.6 (in 2009) to 6.9 (in 2001) with an
  average pH of 6.2 (n = 12). Temperature measurements between August 1998
  and July 2009 range from 11.2C (in 1999) to 22.2C (in 1998) with an average
  temperature of 18C (n = 12). The presence of methane and the high %AN values
  indicate reducing conditions exist in this well, suggesting that the dechlorination
  products observed here were produced nearby.
- Monitoring well H17-M01B penetrates the B aquifer on the northwestern portion
  of the site adjacent to the Delaware River. These samples (n = 14) were collected

between August 1990 and July 2011 (Figure 2-11). During 1994-1998, the partial

dechlorination factor dominated here. Later, from 1998-2011, the advanced

dechlorination factor dominated. This may indicate that the partial dechlorination

regime gave way to the advanced regime as CB accumulated. This observation is

counterintuitive if the same dechlorinator is responsible for dechlorination in well

G05-M02B. It appears there might be different dechlorinators for the partial and

advanced dechlorination regimes in H17-M01B, which is not surprising since

diverse classes of microorganisms mediate subsurface CB-dechlorination.[79]

Alkalinity, ferric iron, ferrous iron, nitrite, sulfide, and methane aqueous

groundwater concentrations are not available for H17-M01B, however sulfate was

measured in the early 1990s (8,900 µg/L, August 1990; 11,500 µg/L, May 1992;

20,700 µg/L , May 1993; 50,000 µg/L, May 1994). %AN data available between

1990 and 2003 show %An values range from 3% (in 2001) to 100% (1990-1994)

with an average of 87% (n = 10). pH measurements are available between 1990-

2011 and range between 6.4 (in 2011) to 7.6 (in 1998) with an average pH of 6.8

(n = 13). Lastly, temperature measurements between 1994 and 2011 show a range

of temperature between 14.2C (in 2011) to 19C (in 1998) with an average

temperature of 16.4C (n = 10) in monitoring well H17-M01B. It is unfortunate

that so little ancillary data is available for this well, but the %AN values suggest

reducing conditions here.

2.3.7 Spatial Trends of Ancillary Measurements

Spatial distribution of absolute concentration of various ancillary measurements was examined using ArcGIS software. Concentration gradients of select geochemical, nutrient, and field data are plotted throughout the wells considered in the study and observations are presented below.

- pH & Alkalinity (ALK): Here, pH and ALK are positively correlated (p = 0.0005, n = 51) There is a large range of pH values in the dataset (Figure 2-12). Areas that are more acidic (pH < 4.9) are scattered throughout the site with some grouping occurring in the center, northwestern perimeter adjacent to the Delaware River as well as the southern portion adjacent to the Salem Canal. Areas with more alkaline (ALK > 180,000 µg/L) groundwater wells appear to occur in the southwestern perimeter as well as northwestern and northeastern portions of the site in areas that are also high in the advanced degradation factor. For example B08-P02B is high in the advanced degradation factor as well as alkalinity (ALK = 375,000 µg/L, March 2008).

- Temperature: The groundwater temperature generally appears to be higher further away from the center and warmer spots appear to make a circular pattern around the site (Figure 2-13). Grouping of wells with higher temperatures (T < 20C) occur on the perimeter near the Delaware River and Salem Canal. Wells with lowest temperature (T > 16C) readings are located further away from the surrounding water bodies. The circular pattern of warmer groundwater temperatures may be explained by the presence of pumping wells, which aim to stabilize contaminant plumes from offsite migration. Wells with warmer

groundwater temperatures (T < 19C) are located near interceptor wells, which may generate heat from continual operation of pumps and/or suck in warmer surface water in these areas. The ladder may be true since the aforementioned pattern is more prominent during warmer months in the spring and summer.

- Total Organic Carbon (TOC): High concentrations of TOC (> 75,000 μ g/L) occur in the northeastern corner of the site in areas that are also high in factor 3 (advanced dechlorination) (Figure 2-13). Since factor 3 correlates with sulfate-reduction, it is interesting to see more TOC in areas high in factor 3 because one might expect to see less TOC where sulfate reduction is occurring.

- Sulfide & Sulfate: Hot spots of sulfide (> 3,800 μ g/L) occur near the perimeter of the site, whereas hot spots of sulfate (> 647,000 μ g/L) occur in the center and northern sections of the site (Figure 2-14). Locations with highl sulfate concentrations (> 114,000 μ g/L; 50th percentile sulfate concentration) might be located near historic gypsum storage sites. Sulfide is high (11,200 μ g/L, June 2011) in monitoring well K10-M01B, which is a B aquifer monitoring well that is high in the advanced dechlorination factor (factor 3). Sulfide is high and sulfate is low in areas that are high in the advanced dechlorination factor, suggesting CB dechlorination is occurring under sulfate-reducing conditions.[30]

- Methane & %AN: The concentration of methane varies across the site (Figure 2-15). Hot spots of methane (> 2,400 μ g/L) mainly occur on the perimeter of the site with few wells in the center. %AN values vary throughout the site with grouping of low values (< 50%) occurring in the northwestern and northeaster corners of the site. Areas with high methane (> 2,400 μ g/L) and high %AN (>

60%) are located in areas that are elevated in the advanced degradation factor indicating the advanced dechlorination regime can take place under a highly reducing environment, which is characteristic of methanogenesis. Mass interceptor well B10-P02B is high in the advanced degradation factor and has elevated concentrations of methane (15,000 μ g/L, March 2008).

2.3.8 Correlation Analysis

Spearman's rank-order correlations were performed in attempt to identify ancillary parameters that are correlated with the various PMF factors, especially factors 2 and 3 which are indicative of dechlorination. When correlations are performed on the ranked absolute concentrations of model output (Table 2-5), the source term (factor 1 containing mostly 1,2-DCB) is positively correlated with methane, sulfate, and TOC and is negatively correlated with pH. The partial degradation term (factor 2, CB) is positively correlated with alkalinity, methane, sulfate, TOC, and fraction of aniline (%), and is negatively correlated with pH. The advanced dechlorination term (factor 3, 1:3 CB:B) is positively correlated with alkalinity, methane, nitrite, sulfate, TOC, and %AN, and is negatively correlated with temperature and pH. The fact that all three factors are positively correlated with sulfate and methane is confusing and sheds no light on which dechlorination regimes occur under which conditions.

Correlations performed on the *relative* concentration of each factor in each sample were more helpful (Table 2-5): the source term (factor 1) is positively correlated with redox and negatively correlated with ferrous iron, ferric iron, sulfate, pH, and the fraction of

aniline (%). The partial dechlorination term is positively correlated with sulfate and

temperature and negatively correlated with nitrite and TOC. Lastly, the advanced

dechlorination term is positively correlated with alkalinity, ferrous iron, methane, nitrite,

sulfide, TOC, and the fraction of aniline (%) and negatively correlated with sulfate and

temperature. Thus the correlations performed on *relative* concentrations of the PMF

factors do reveal useful information about which dechlorination regimes occur under

which conditions: i.e. these results suggest that the partial dechlorination regime is more

likely to occur under sulfate reducing conditions, while the advanced dechlorination

regime is more likely to occur under more deeply reducing conditions, including

methanogenic conditions. In addition the advanced dechlorination term is positively

correlated with TOC, which drives dechlorination. Furthermore, the source term is

correlated with indicators of relatively oxidizing conditions. Thus it appears that the

correlations performed on relative concentrations of the PMF factors are more useful than

those performed on absolute concentrations of the PMF factors *as well as* those

performed on either absolute or relative concentrations of the raw analyte concentrations.

This suggests that the PMF analysis does aid our understanding of the system relative to

close examination of the concentration data without performing factor analysis. The fact

that the PMF output reveals a rational and cohesive story of microbial dechlorination in

the subsurface addresses the final objective (goal d) of the work.

2.4 Implications

Analysis of the chlorinated benzene dataset provided evidence of degradation via

microbial dechlorination in the subsurface. PMF analysis of the chlorinated benzene

groundwater monitoring data resolves the heterogeneous dataset into three factors

representing parent contaminants and two different extents of dechlorination. Two dechlorination signals are identified, which suggests that there may be two pathways for dechlorination, or different microbial populations are responsible or that one of the dechlorination factors represents a more advanced stage of reductive dechlorination than the other. The PMF model output can also be used to estimate how much of the mass of these compounds comes from dechlorination versus how much is attributable to other sources, such as use on site. The solution indicates that nearly all of the monochlorobenzene and benzene in the subsurface is attributable to dechlorination.

Correlation results show the source term is associated with oxidizing (aerobic) subsurface conditions, whereas dechlorination factors are observed under reducing (anaerobic) conditions. The correlation results suggest achieving an advanced stage (factor 3) of chlorinated benzene dechlorination requires methanogenic conditions. The novel approach presented here has also proven useful from a remediation point-of-view. With this more intimate data analysis approach, we can guide bioremediation efforts by obtaining a better understanding as to what is actually happening to chlorinated benzenes in the groundwater onsite. Many bioremediation efforts aim to apply an array of redox environments in order to achieve complete degradation of organic contaminants. The data presented here suggests complete CB-dechlorination requires methanogenic conditions, therefore remediation personnel should try to drive the redox potential down in order to achieve highly-reducing conditions suitable for the advanced reductive dechlorination regime to take place.

Well location map
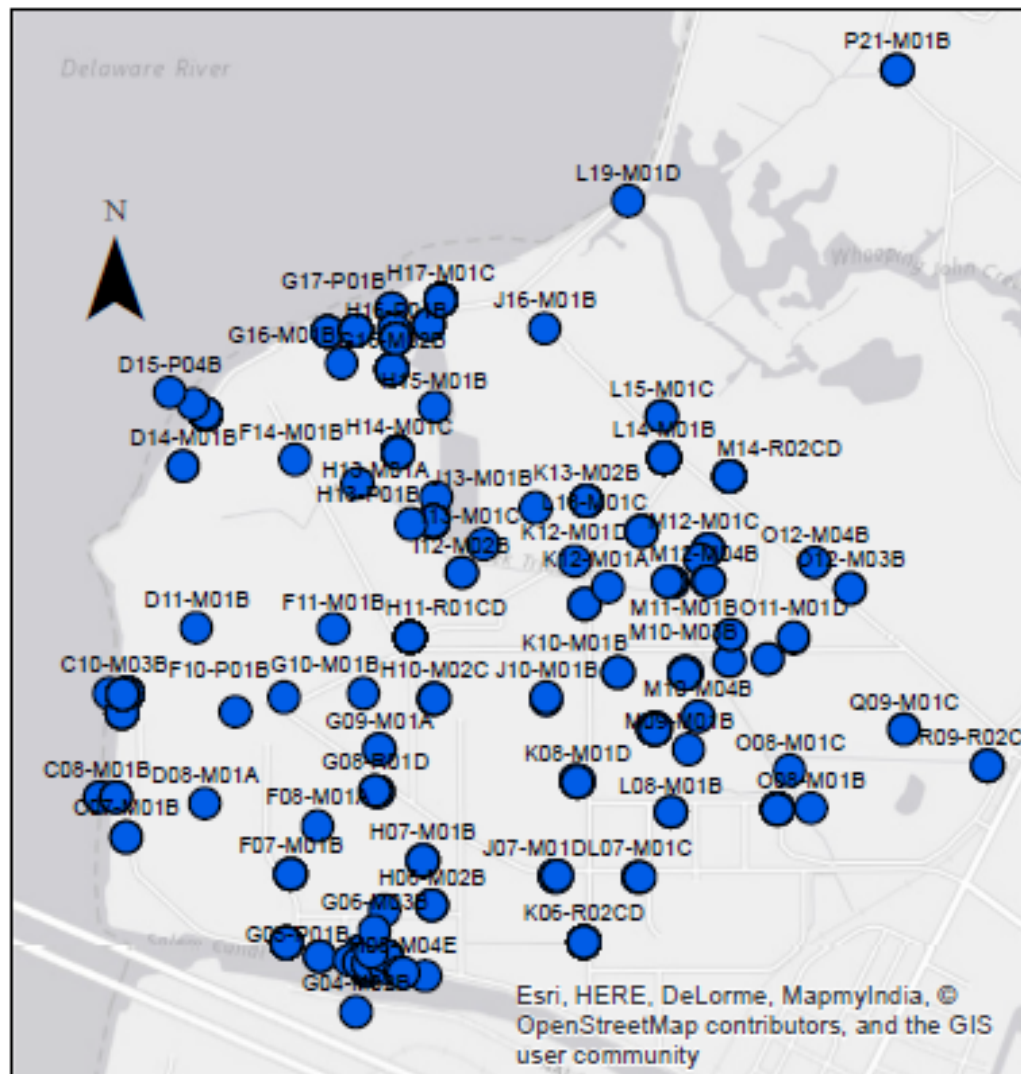
Figure 2-1 Map of the site displaying the layout of the monitoring wells (blue dots) considered in the PMF2 investigation.
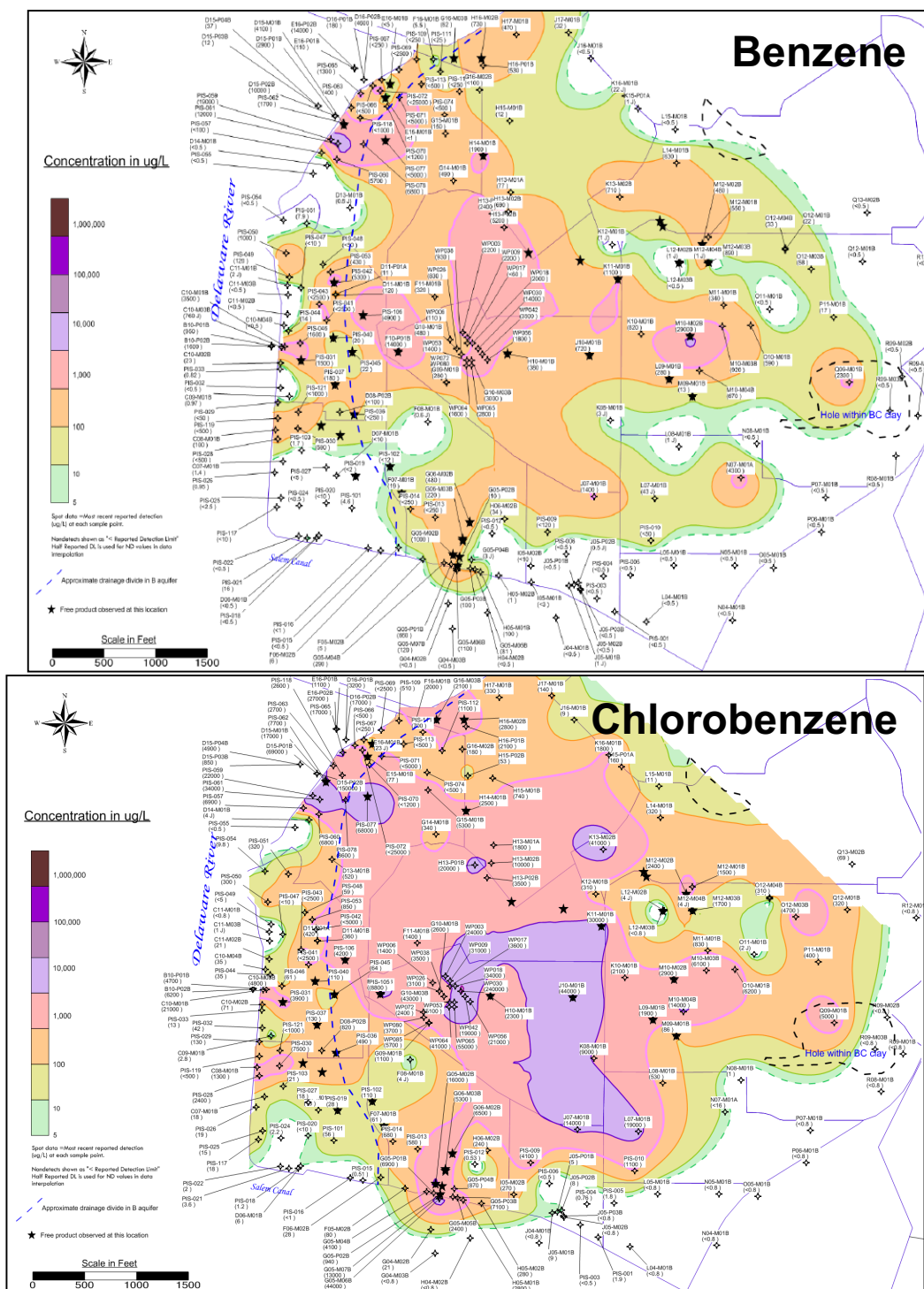
Figure 2-2 Groundwater plumes of the chlorinated benzenes located measured in the B-aquifer onsite. Maps prepared by URS on September 19, 2011 for an internal investigation report.[80]
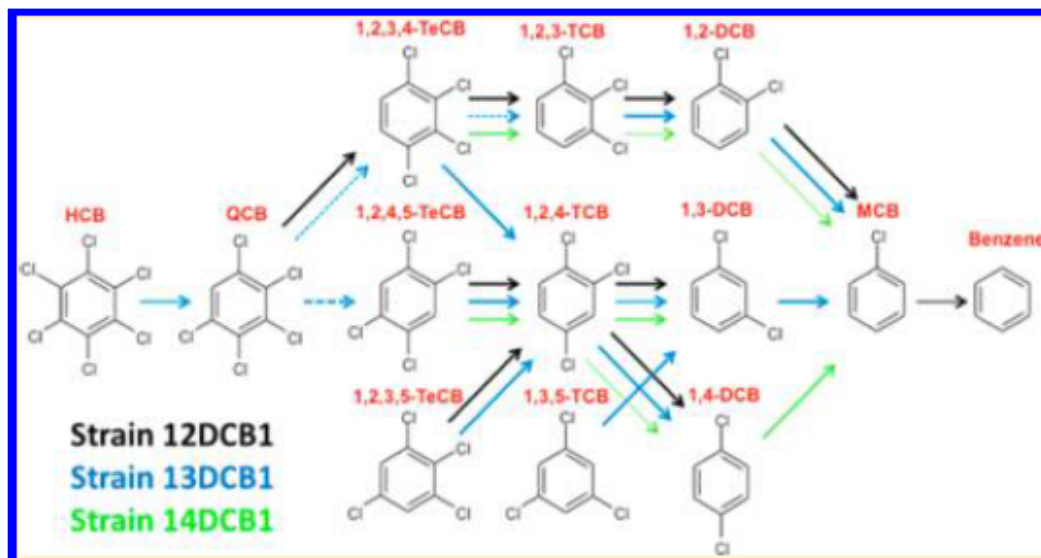
Figure 2-3 Reductive dechlorination pathways of chlorinated benzenes for three isolated strains of *Dehalobacter* spp. from the former Chamber Works facility.[30] Strain 12DCB1, 13DCB, and 14DCB is indicated by a black, blue, green line, respectively.[30] Dashed lines indicate steps not directly detected because of lack of intermediates and thin arrows indicate dechlorination that occurred at low rates.[30]
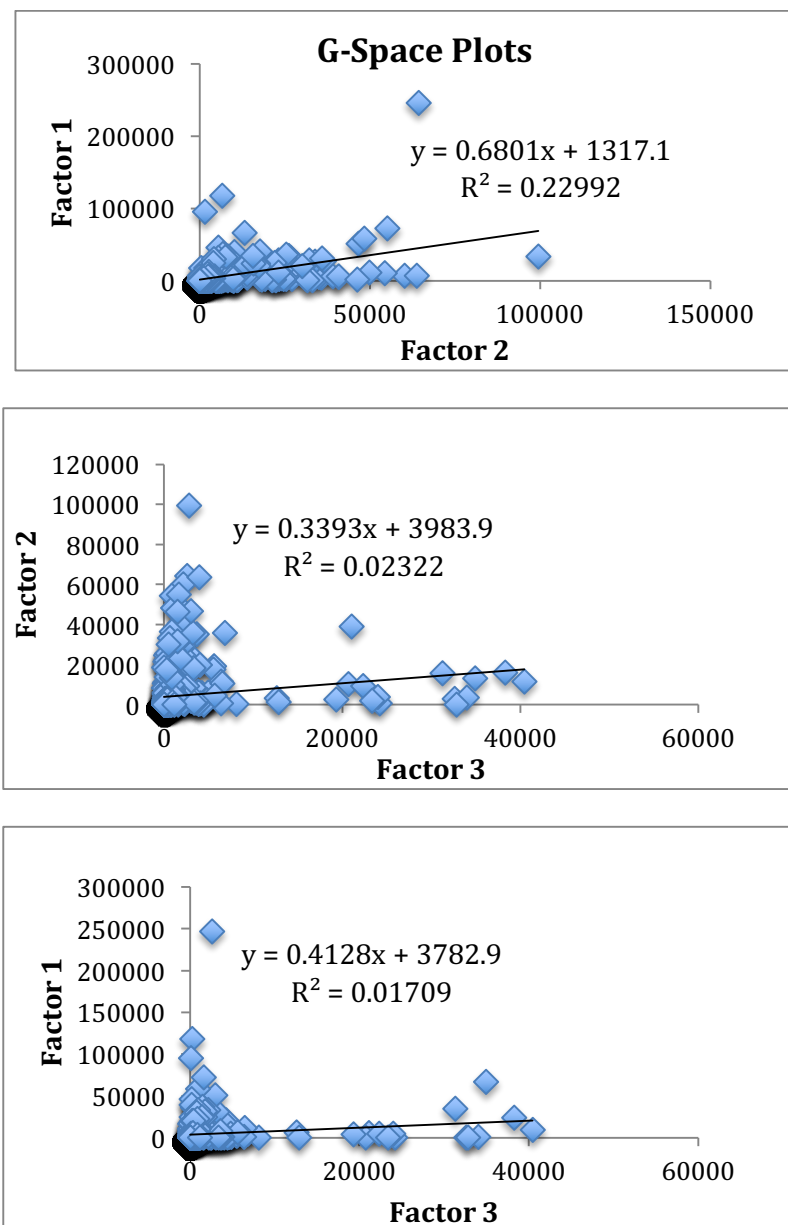
Figure 2-4 G-space plots: pair-wise comparison of the factors for the 3-factor PMF solution. When factors are independent of each other, there should be no correlation between the X and Y of each plot. The plots show a wide scatter of point with many points on and near the X-axis and Y-axis, indicating that the factors are independent of each other and rotation of the data matrix is not required.
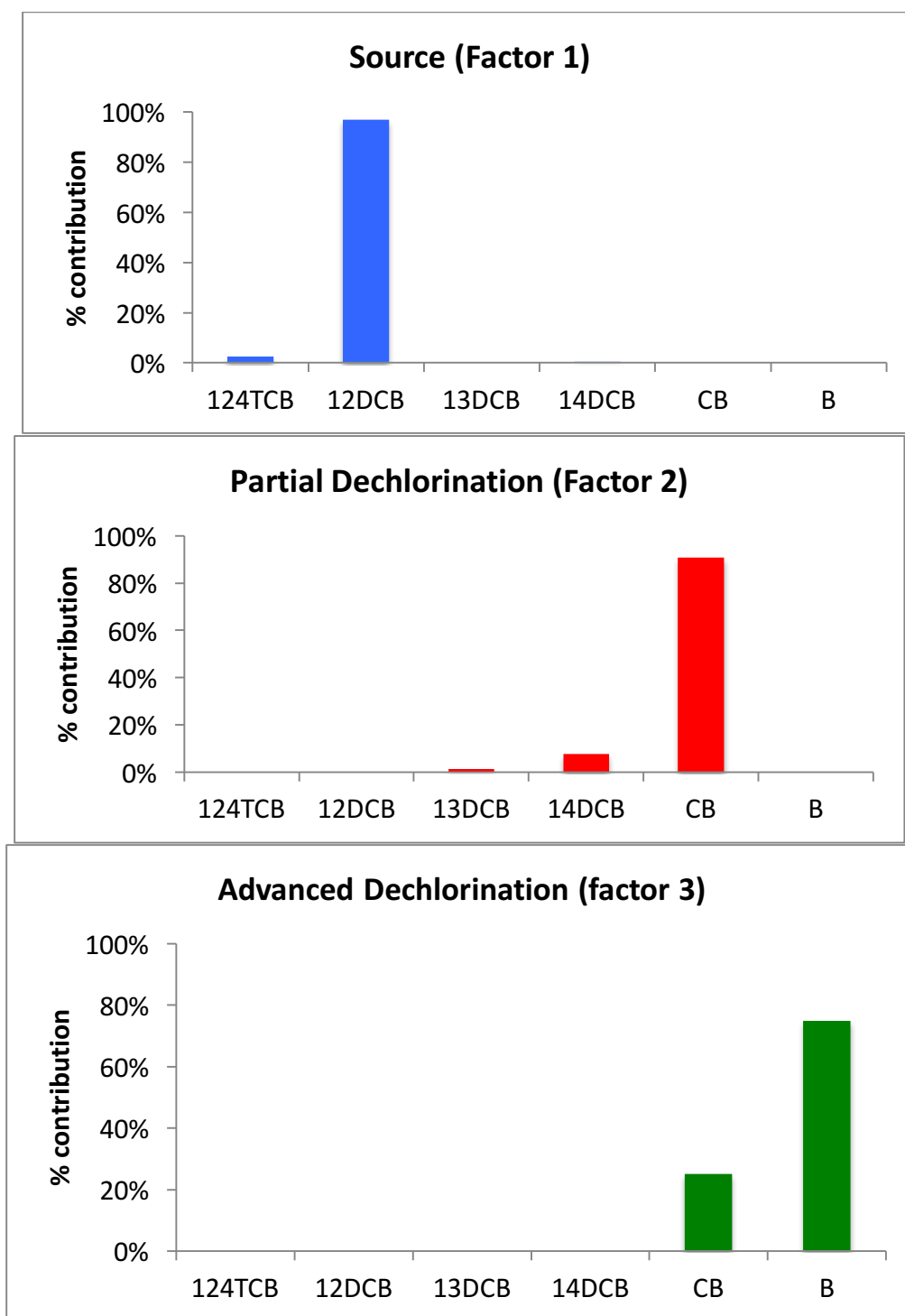
Figure 2-5 Source profiles (fingerprints) of the 3-factors generated by PMF modeling. Percentages indicate the contribution of each analyte to the factor model.
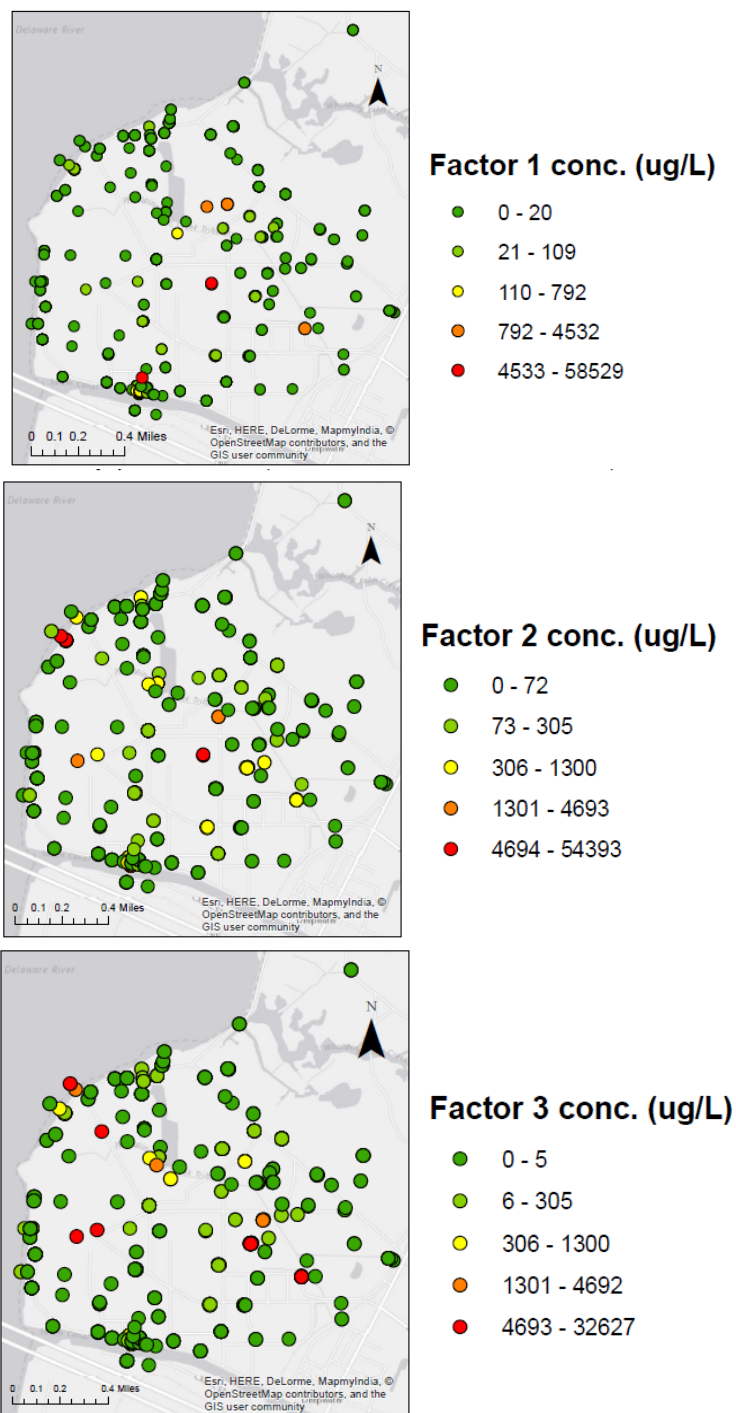
Figure 2-6. The average absolute concentration (ug/L) of each factor profile in wells throughout all years considered (1990- 2011) (factor 1 = source, factor 2 = partial dechlorination, and factor 3 = advanced dechlorination). The scale for the legend was set up in percentiles (e.g., 20th, 40th, 60th, 80th, and 99th).
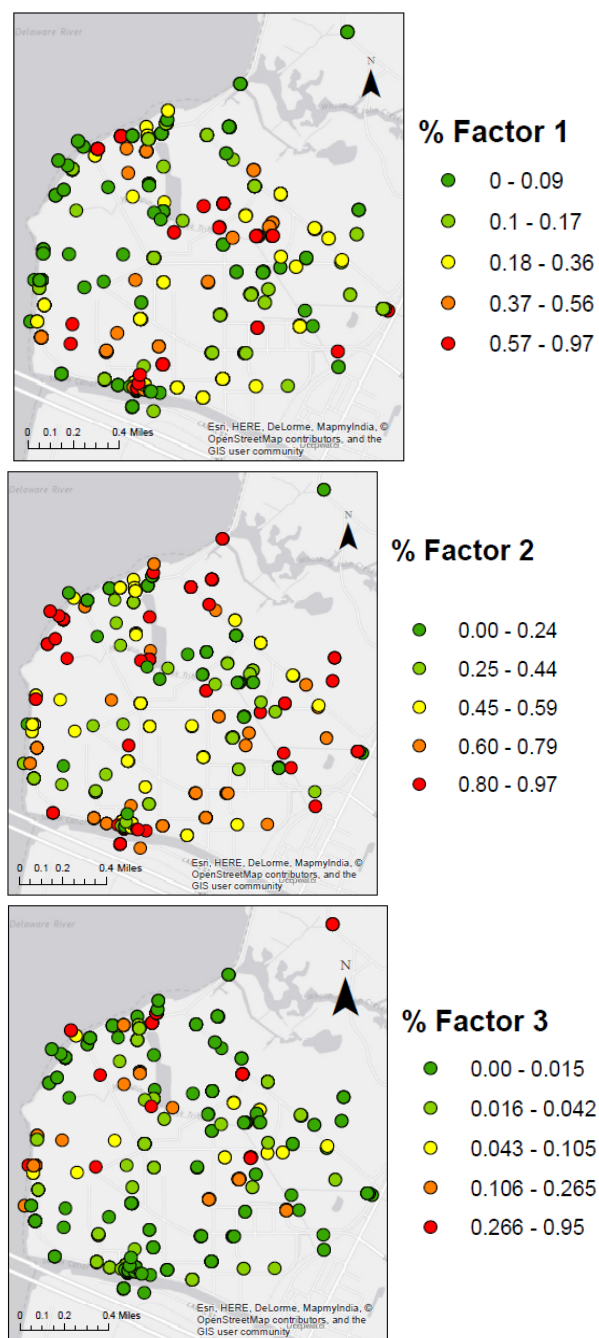
Figure 2-7. **The percent of the total mass contribution (*relative* concentrations of the G-matrix) of each factor in each well is displayed throughout the study period (1990- 2011) (factor 1 = source, factor 2 = partial dechlorination, and factor 3 = advanced dechlorination). The scale for the legend was set up in percentiles (e.g., 20th, 40th, 60th, 80th, and 99th).**
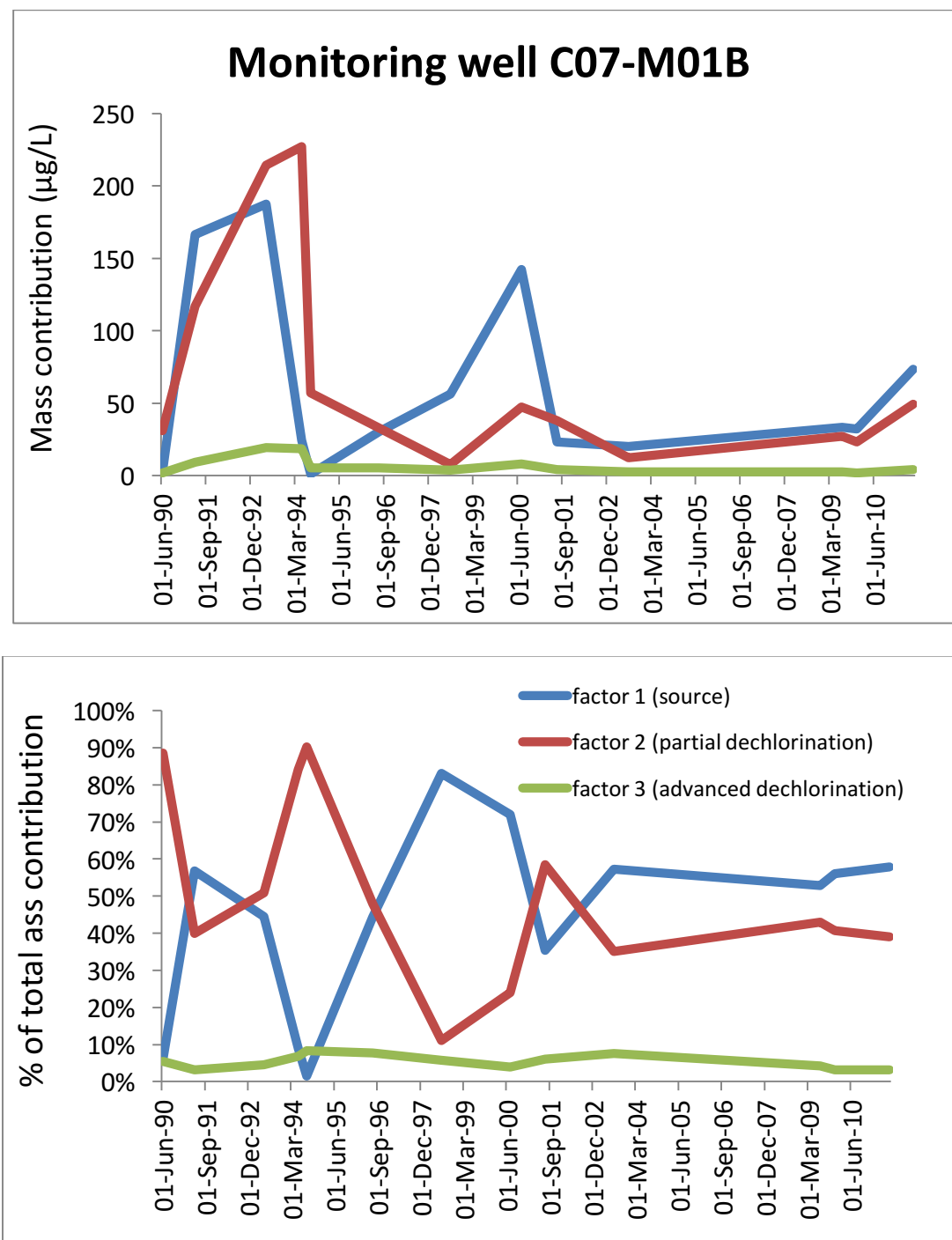
Figure 2-8. Plot of the absolute concentration (μg/L) and *relative* concentration (% of total mass) of the mass contribution (G-matrix) of the model output in monitoring well C07-M01B between the years 1990 and 2011.
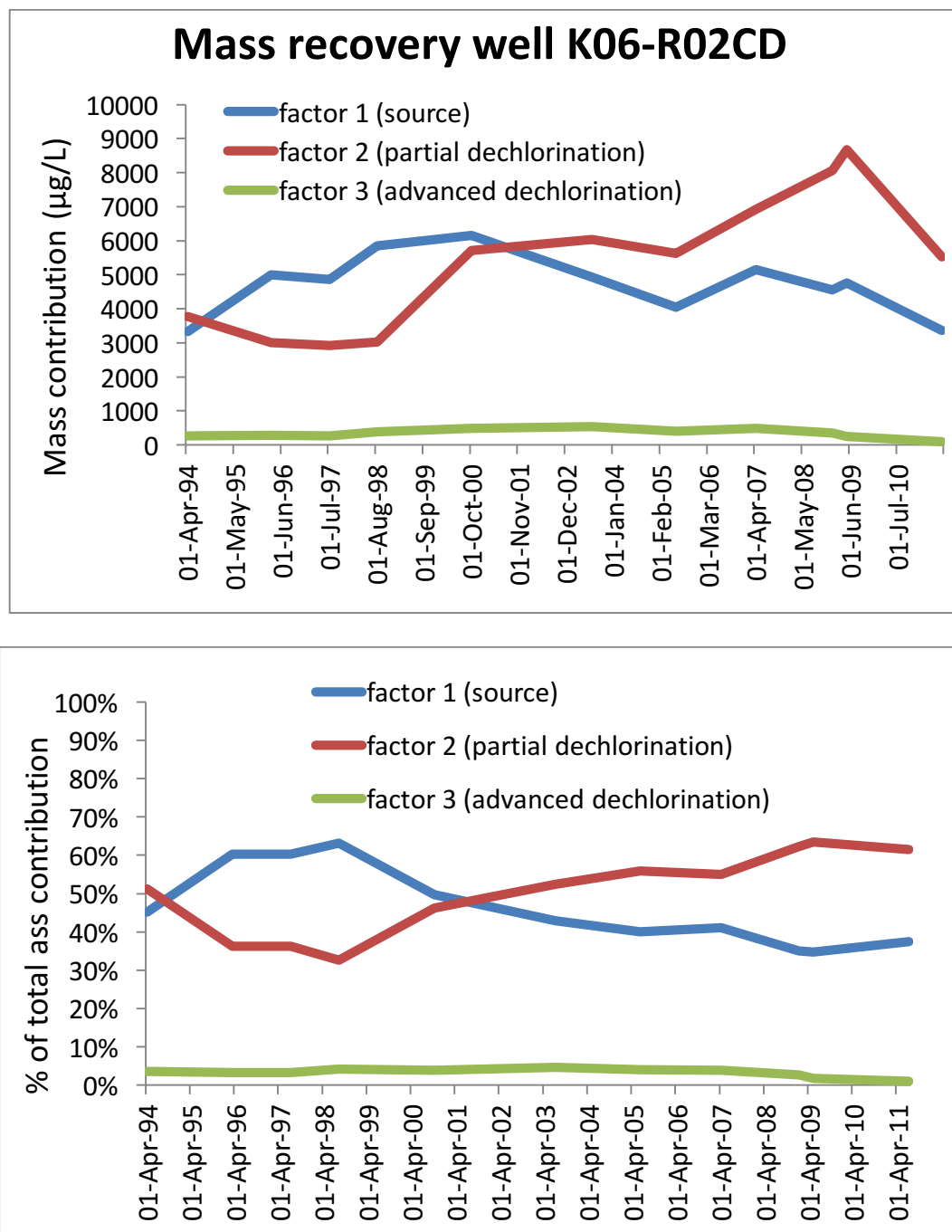
Figure 2-9. **Plot of the absolute concentration (µg/L) and *relative* concentration (% of total mass) of the mass contribution (G-matrix) of the model output in mass recovery well K06-R0CD between the years 1990 and 2011.**
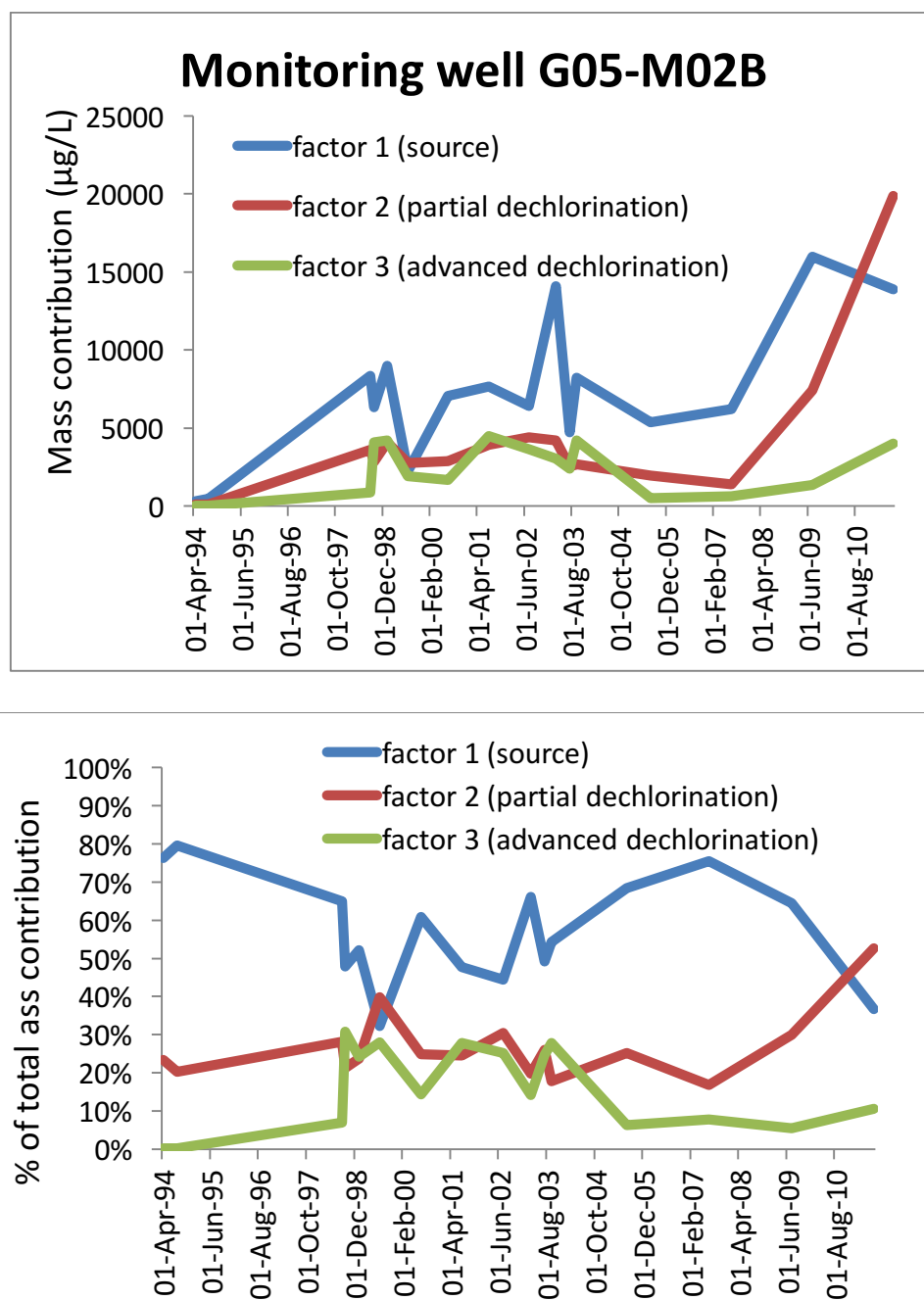
Figure 2-10. Plot of the absolute concentration (µg/L) and *relative* concentration (% of total mass) of the mass contribution (G-matrix) of the model output in monitoring well G05-M02B between the years 1994 and 2011.
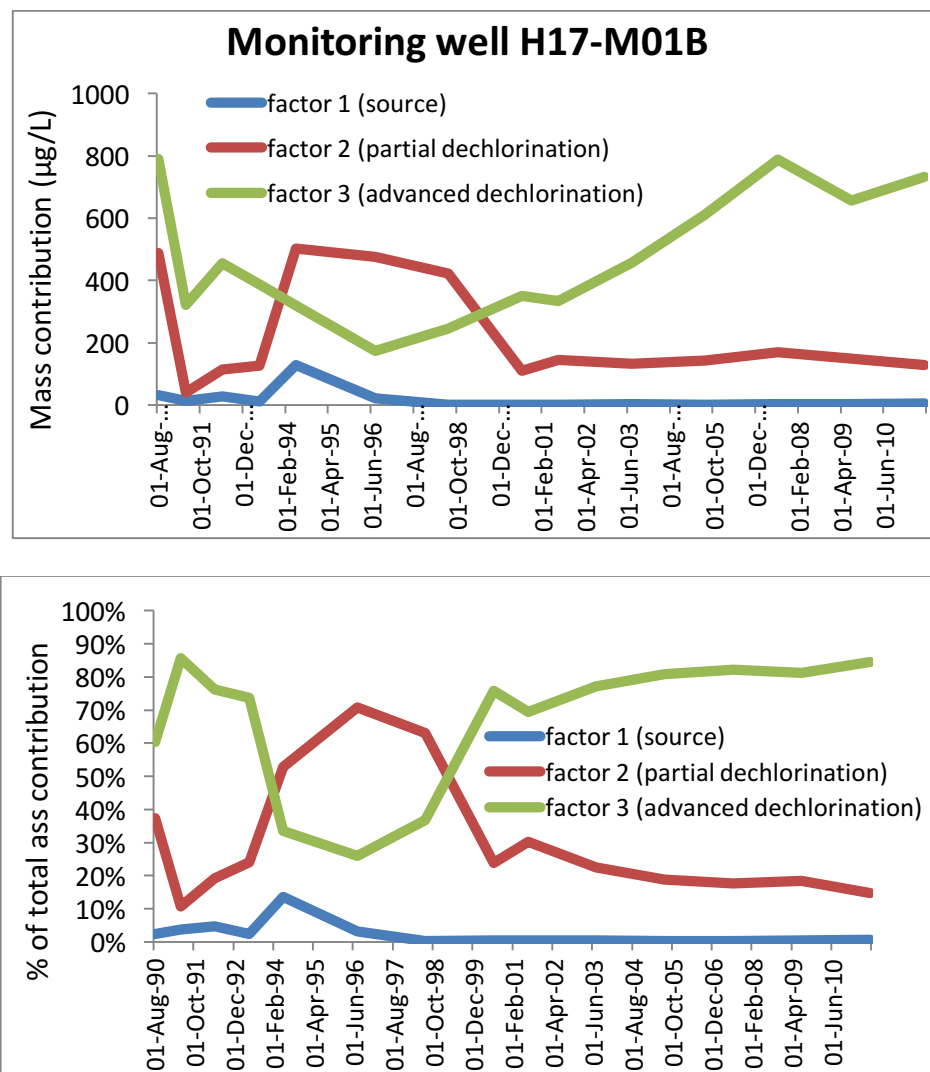
Figure 2-11. Plot of the absolute concentration (µg/L) and *relative* concentration (% of total mass) of the mass contribution (G-matrix) of the model output in well H17-M01B between the years 1990 and 2011.
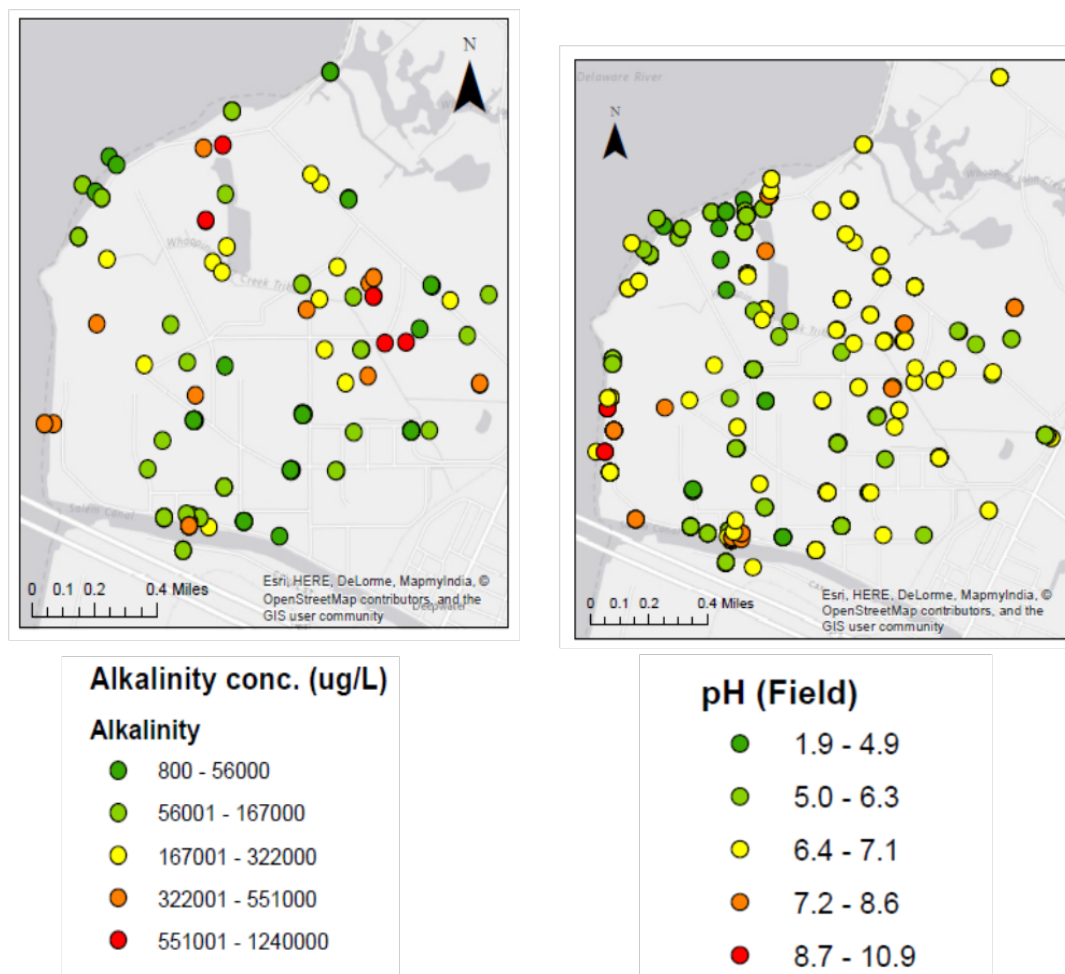
Figure 2-12. Average pH and alkalinity (µg/L) in monitoring wells considered in the chlorinated benzene factor analysis solution.
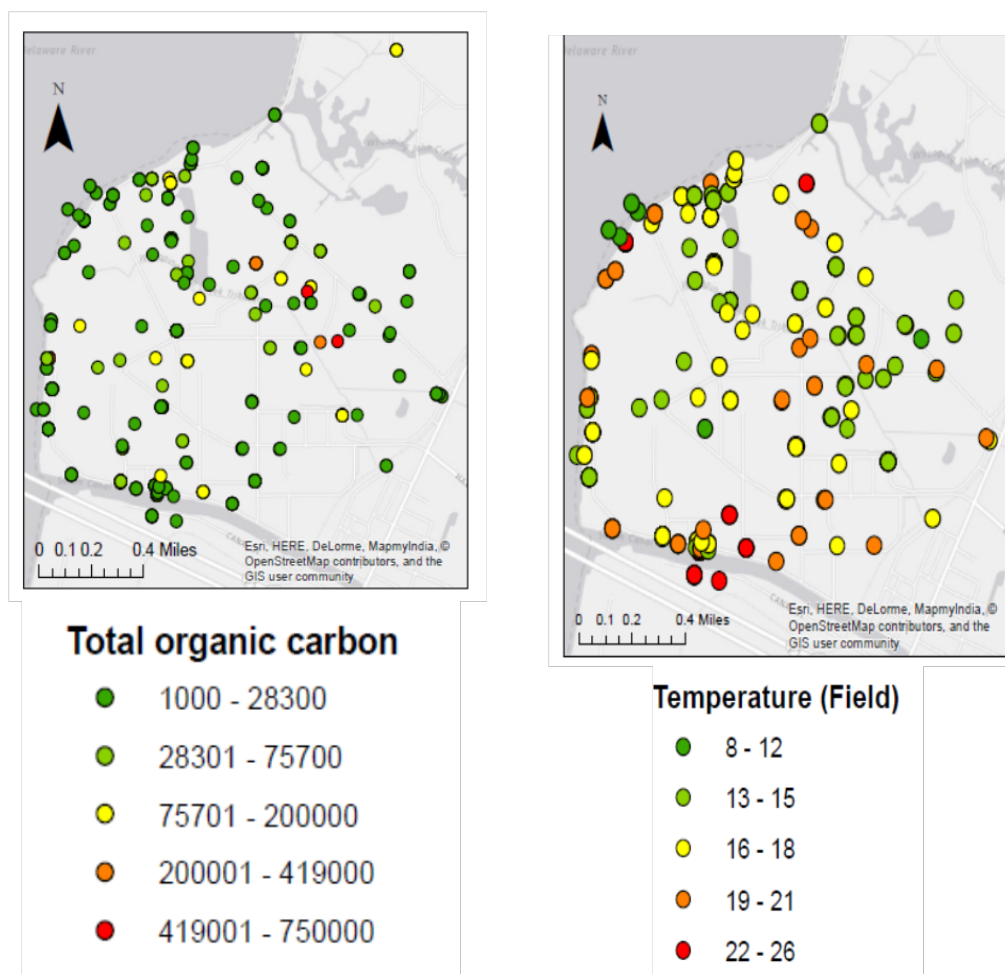
Figure 2-13. Average temperatures (ºC) and total organic carbon (TOC, μg/L) in monitoring wells considered in the chlorinated benzene factor analysis solution.
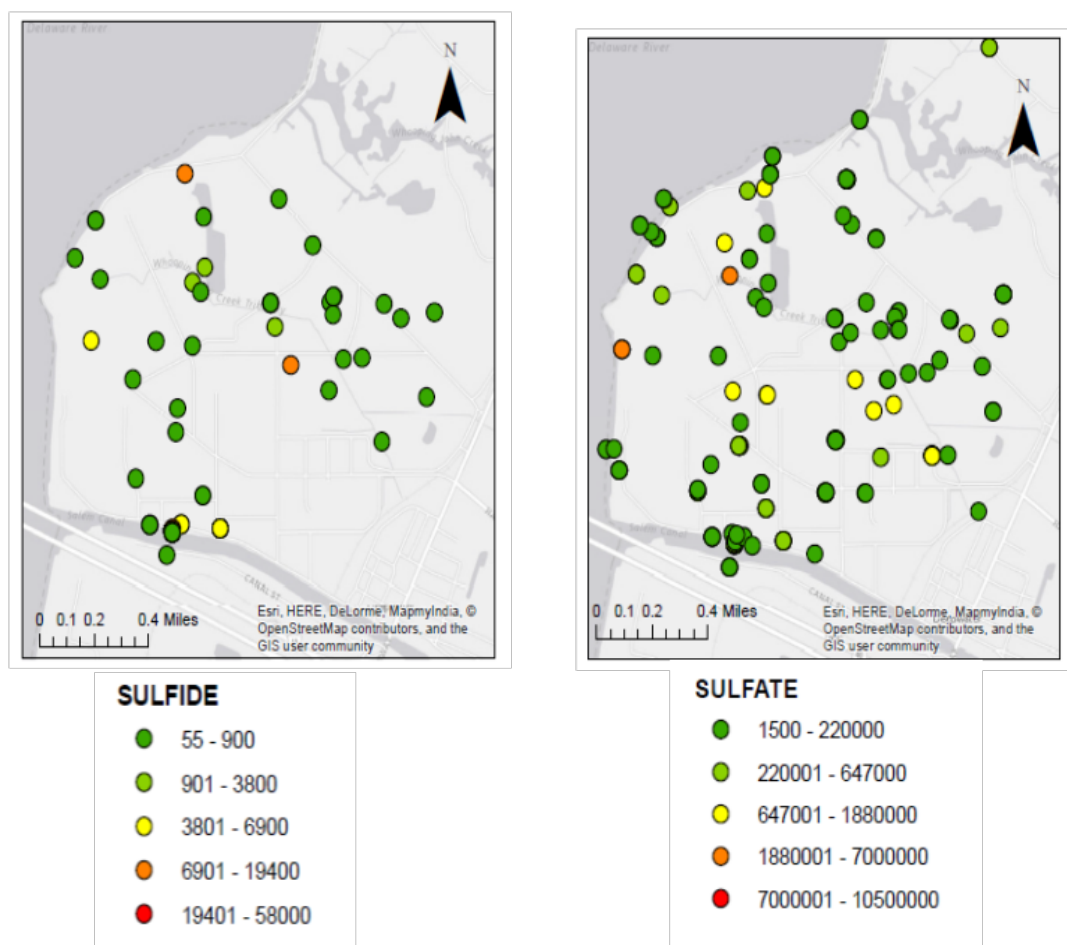
Figure 2-14. The average concentration (ug/L) of sulfate and sulfide (μg/L) in monitoring wells considered in the chlorinated benzene factor analysis solution.
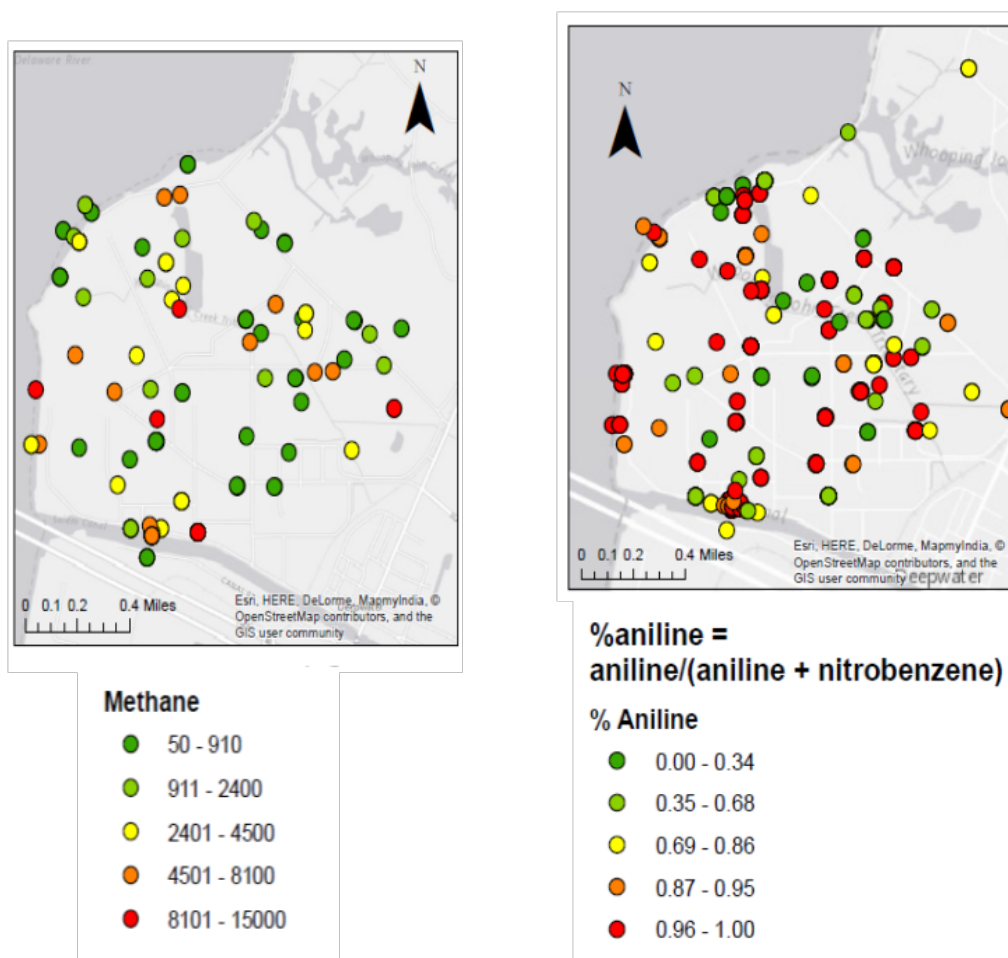
Figure 2-15. The average concentration of methane (µg/L) and the fraction of aniline (%AN) as the sum of aniline and nitrobenzene in monitoring wells considered in the chlorinated benzene factor analysis solution.

Table 2-1. The 5 chlorinated benzenes and benzene included in the PMF investigation and their molecular weight, octanol-water partitioning coefficient, LogK$_{ow}$, Henry law constant, K$_H$, and chemical structures. MW, log K$_{ow}$, and K$_H$ values obtained from U.S. EPA KOWWIN software version 1.67.
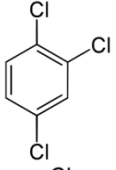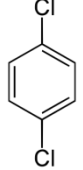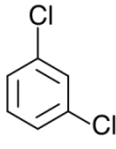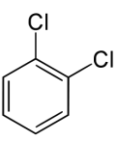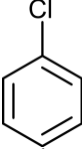
Chemical Name	MW	Log K$_{ow}$	Henry's Law Constant K$_H$ at 25ºC (atm*m^3/mole)	Chemical Structure
1,2,4-Trichlorobenzene (1,2,4-TCB)	181.45	4.06	1.42×10^{-3} (experimental)	
1,4-Dichlorobenzene (1,4-DCB)	147.01	3.45	1.92×10^{-3} (experimental)	
1,3-Dichlorobenzene (1,3-DCB)	147.01	3.47	2.63×10^{-3} (experimental)	
1,2-Dichlorobenzene (1,2-DCB)	147.01	3.40	2.41×10^{-3} (experimental)	
Monochlorobenzene (CB)	112.56	2.78	3.11×10^{-3} (experimental)	
Benzene	78.11	2.17	5.55×10^{-3} (experimental)	

Table 2-2 Distribution of chlorinated benzenes and ancillary concentration data regarding each analyte in the 597 aqueous groundwater samples collected from over 140 wells included in the PMF model. The 10th, 50th, and 90th percentile concentrations (the Xth percentile concentration is that for which X% of the measured concentrations were lower) are reported for each analyte after preprocessing the data matrix for PMF analysis.

	10th %ile	50th %ile	90th %ile	Minimum detected conc.	Maximum detected conc.	Mean
Alkalinity (μg/L)	228	108,500	382,800	15	124,000	178,133.5
TOC (μg/L)	4,390	17,700	99,290	1,000	750,000	44,826.9
Ferrous iron (μg/L)	460	6,200	63,100	28	173,000	24,369.0
Ferric iron (μg/L)	1,300	15,700	75,360	200	944,000	62,232.5
Methane(μg/L)	73	1,600	6,740	6	15,000	2,665.7
Nitrite (μg/L)	30	73.5	200	16	900	119.8
Nitrate (μg/L)	168	510	3,100	44	13,500	1,500.4
Sulfate (μg/L)	19,800	114,000	909,000	1,500	10,500,000	385,425.6
Sulfide (μg/L)	80	620	7,980	55	58,000	3,444.6
Temperature (ºC)	13.2	16.8	20.5	7.8	26.1	17.0
pH	5.5	6.4	7.5	1.9	11.0	6.0
pE (mV)	-129.7	-49.5	86.3	-373.4	397.8	-35
Aniline (μg/L)	4	420	19,400	1	460,000	8,911.0
Nitrobenzene (μg/L)	5	320	29,000	1	740,000	13,820.0
1,2,4-TCB(μg/L)	2	76	1,480	1	630,000	2,658.9
1,2-DCB (μg/L)	9	340	11,000	1	230,000	4,753.6
1,3-DCB(μg/L)	2	31	410	0.6	2,300	126.8
1,4-DCB (μg/L)	3	72	1,380	0.6	49,000	615.2
CB (μg/L)	30	1,000	19,700	1	78,000	6,138.9
Benzene (μg/L)	3	110	2,230	0.5	51,000	1,186.3

Table 2-3 Spearman's Rank-Order Correlations for measured chlorinated benzenes: the rank of absolute concentration [C] and the rank of percent of total mass (%) of each factor versus the rank of ancillary parameters after preprocessing the data matrix for PMF analysis. For those significant trends where p < 0.05, pink sign indicates a positive correlation, light blue indicates a negative correlation and no correlation are reported as yellow.   For those significant trends where p < 0.005, red indicates a positive correlations and dark blue indicates a negative correlation and no correlation is reported as yellow. Note the units of ancillary parameters are ug/L except for T (C), pH, pE, and %AN, which are unitless.

	n	1,2,4-TB [C]	%	1,2-DCB [C]	%	1,3-DCB [C]	%	1,4-DCB [C]	%	CB [C]	%	Benzene [C]	%
pE	320	yellow	yellow	yellow	yellow	yellow	dark blue	yellow	yellow	yellow	yellow	yellow	yellow
Nitrate	33	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow
Nitrite	74	yellow	yellow	yellow	yellow	yellow	light blue	yellow	yellow	yellow	yellow	pink	pink
%AN	418	yellow	dark blue	yellow	dark blue	yellow	light blue	pink	red	red	red	red	red
Ferric	63	yellow	yellow	yellow	light blue	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow
Ferrous	71	dark blue	yellow	yellow	yellow	light blue	dark blue	yellow	yellow	yellow	yellow	yellow	pink
Sulfate	191	pink	yellow	red	red	pink	yellow	red	light blue	pink	light blue	pink	yellow
Sulfide	67	yellow	yellow	yellow	yellow	yellow	yellow	pink	yellow	yellow	yellow	yellow	light blue
Methane	127	yellow	dark blue	red	yellow	yellow	dark blue	red	yellow	red	yellow	red	yellow
pH	470	yellow	red	dark blue	light blue	yellow	red	light blue	yellow	dark blue	yellow	light blue	yellow
T	401	yellow	yellow	yellow	yellow	yellow	pink	yellow	yellow	yellow	yellow	dark blue	yellow
TOC	500	red	dark blue	red	yellow	red	dark blue	red	yellow	red	yellow	red	red
Alkalinity	144	yellow	light blue	yellow	yellow	yellow	yellow	yellow	yellow	red	yellow	red	pink

Table 2-4 The relative standard deviation (RSD) of the G-matrix for model

outputs requesting different numbers of factors, RSD of 10 model runs with random

seed values.

Number of Factors	RSD of G Matrix (%)
2	2.2%
3	0.6%
4	76.5%
5	0.8%
6	0.4%

Table 2-5 Spearman's Rank-Order Correlations on model output: the rank of absolute concentration and percent of total mass of each factor versus the rank of ancillary parameters after preprocessing the data matrix for PMF analysis. For those significant trends where p < 0.05, pink sign indicates a positive correlation, light blue indicates a negative correlation and no correlation are reported as yellow. For those significant trends where p < 0.005, red indicates a positive correlations and dark blue indicates a negative correlation and no correlation is reported as yellow. Note the units of ancillary parameters are ug/L except for T (C), pH, pE, and %AN.

	n	Source (factor 1) [C]	%	Partial Dechlorination (factor 2) [C]	%	Advanced Dechlorination (factor 3) [C]	%
pE	320						
Nitrate	33						
Nitrite	74						
%AN	418						
Ferric	63						
Ferrous	71						
Sulfate	191						
Sulfide	67						
Methane	127						
pH	470						
T	401						
TOC	500						
Alkalinity	144						

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Chapter 3: Chlorinated Ethenes

Abstract

Chlorinated ethenes are among the most common groundwater contaminants in the United States, and demonstrating whether they undergo degradation in the subsurface is important in determining the best remedy for this contamination. The purpose of this work was to use a new approach to investigate chlorinated ethene degradation pathways in the subsurface. Positive Matrix Factorization (PMF) was applied to historical monitoring data regarding chlorinated ethenes measured in groundwater at the Chambers Works facility in order to consolidate observations into a smaller number of more easily interpreted factors. A dataset containing concentrations of 6 chlorinated ethenes and breakdown products in 76 aqueous groundwater samples collected in over 40 wells, throughout 2005 and 2011, was investigated using PMF2 software. Despite the many shortcomings of this dataset, including missing analytes, quality assurance parameters, and method information, PMF analysis revealed a logical story of microbial dechlorination in the groundwater which provides insight as to where dechlorination is occurring, to what extent and under which conditions. PMF resolved a factor indicative of a source of tetrachloroethene and trichloroethene and two factors representing stages of dechlorination, one more advanced than the other. Factors were further interpreted using ancillary data such as redox indicators and field parameters also measured in the samples. Analysis suggested that the partial and advanced dechlorination signals occur under different environmental conditions. The results provided field validation of the current understanding of anaerobic dechlorination of chlorinated ethenes in the

subsurface gleaned from laboratory studies. Specifically, partial dechlorination of tetrachloroethene to dichloroethene appears to occur under iron or sulfate-reducing conditions, whereas the advanced dechlorination regime of vinyl chloride to ethene and ethane appears to require methanogenic conditions. PMF has been shown to be a useful tool for investigating chlorinated ethene dechlorination despite the heterogeneity of groundwater monitoring data.

3.1 Introduction

Chlorinated ethenes, such as tetrachloroethene (PCE) and trichloroethene (TCE), are widespread groundwater contaminants.[1-4] Chlorinated solvents are used in many industrial and commercial applications in the United States.[1-4] PCE is used as a dry cleaning solvent, chemical intermediate, metal cleaner, and a vapor degreaser.[1-4] PCE was used at the Chambers Works facility to make fluorinated products such as Freon® and is one of the primary organic pollutants detected in the subsurface at Chambers Works. A site location map of the Chambers Works complex is displayed in Figure 1-1. Chlorinated ethene (CE) contamination is prominent in the groundwater in the southern portions of the site (Figure 3-1). Open wastewater ditches and trenches were historically used to convey spent solvents or byproducts from chemical manufacturing processes. This former conveyance method caused the inadvertent release of pollutants to underlying sediment and groundwater since the systems were either unlined or poorly engineered at the time. The disposal of processed waste via trench systems ended in 1974 with the creation of a closed sewer system that transports waste to an on-site wastewater treatment facility.

3.1.1 Properties of Chlorinated Ethenes

PCE and TCE are persistent in soil and slightly soluble in water, causing them to be especially problematic in subsurface systems.[5] PCE, TCE, and dichloroethylene (DCE) isomers are classified as a Dense Non-Aqueous Phase Liquids (DNAPL) and tend to sink to the bottom of aquifers at or near the point of entry, creating liquid pools of product that gradually dissolve into the groundwater.[5] Chlorinated ethenes are semi-volatile organic compounds (SVOCs) and therefore can partition into the air compartment, causing issues with vapor intrusion in overlying structures. The US EPA recognizes PCE, TCE, 1,1-DCE, and vinyl chloride (VC) as a hazardous air pollutants under the Clean Air Act. In addition, PCE, TCE, *trans*DCE, 1,1-DCE, and VC are listed on the Priority Toxic Pollutants list under the Clean Water Act.[6] Furthermore, chlorinated ethenes are recognized as a hazardous substances under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and, therefore, stringent remedial standards must be adhered to for any reported contamination.[6]

Chlorinated ethenes have been linked to numerous adverse health effects in epidemiological studies. Acute inhalation of PCE and TCE vapors causes central nervous system depression as well as irritation to the upper respiratory tract, eyes, nose and throat.[7] Chronic exposure to PCE and TCE can cause damage to the liver, kidneys, and reproductive system.[7] Adverse neurological effects such as memory loss and confusion have also been reported in cases of repeated exposure to PCE.[7] In addition, epidemiological studies suggest exposure to PCE and TCE may lead to an increased risk for a variety of cancers.[7] Remediation of chlorinated ethene contamination poses a

special problem, as transformation products are just as, or even more toxic than parent compounds. TCE is a suspected human carcinogen, DCE isomers are 50 times more hazardous than TCE (in terms of toxicity), and VC is a known carcinogen and has been implicated in liver disease.[6-8]

3.1.2 Reaction Pathways of Chlorinated Ethenes

In order to prevent human exposure to VC, mineralization or complete dechlorination to innocuous ethene is the desired result of remediating CE contaminated systems. Both biotic and abiotic processes determine the fate of chlorinated ethenes. In most groundwater systems, PCE and TCE undergo reductive dechlorination under anaerobic conditions (Figure 3-2). PCE and TCE are susceptible to biotic reductive dechlorination by microorganisms as well as abiotic reductive dechlorination by reduced minerals such as iron sulfide (FeS).[9, 10] The pathways of this abiotic dechlorination can be complex. PCE can undergo reductive beta-elimination to yield chloroacetylene and eventually ethene and ethane.[9] Reductive beta-elimination takes place when two chlorine atoms are released accompanied by the formation of a carbon-carbon bond. This elimination pathway can circumvent the production of vinyl chloride, which is particularly toxic. The reductive elimination pathway has been observed in laboratory settings using abiotic reagents[9, 11], but to date there has been no evidence that it occurs in groundwater. Alternatively, dechlorination by sequential hydrogenolysis can result in chlorinated ethenes with fewer chlorines such as DCE or VC.[9] Hydrogenolysis occurs when the chlorine atom is replaced by a hydrogen atom, which is accompanied by the addition of two electrons.

Previous studies have displayed the ability of microorganisms to sequentially

dechlorinate PCE under anaerobic conditions using a variety of electron donors.[12-15]

This sequential removal of chlorine atoms under anaerobic conditions is often referred to

as anaerobic reductive dechlorination.[13-22] When coupled to energy generation the

process is referred to as organohalide respiration.[23] During reductive dechlorination of

TCE, *cis*-1,2-dichloroethene (*cis*DCE) is the major isomer produced, while *trans*-1,2-

dichloroethene (*trans*DCE) is reportedly more resistant to anaerobic dechlorination.[16]

The final dechlorination of VC to ethene is the most difficult step to achieve and few

microbes (e.g., *Dehalococcoides* spp.) are reported to have the ability to perform this

step.[13, 16, 24] Researchers have sought to better understand the mechanisms of PCE

dechlorination and identify strains of microorganisms capable of mediating the complete

dechlorination of PCE to ethene. Biotic reductive dechlorination of PCE in subsurface

environments encompasses both organohalide respiration and cometabolic

dechlorination. Organohalide respiration is commonly observed and is a metabolic

reaction where energy is gained.[19, 23, 25] In contrast, cometabolic dechlorination is a

nonspecific, fortuitous side reaction not coupled to energy gain.[19, 25] PCE-

dechlorinating microorganisms include a handful of phylogenetically different bacteria

such as dehalorespiring bacteria and sulfate-reducing bacteria.[12-14, 16, 26]

3.1.3 Goals of This Work

Thus the goals of this work are to: a) determine whether data of this quality can be

successfully analyzed by PMF; b) determine whether PMF can give useful information of

microbial dechlorination processes in groundwater; c) investigate where and when microbial dechlorination of chlorinated ethenes occurred in the subsurface at Chambers Works; and d) investigate correlations between PMF outputs related to microbial dechlorination and ancillary parameters such as temperature, redox indicators and alkalinity in order to understand which conditions favor microbial dechlorination. We know microbial dechlorination is occurring at the site[27], which is why we are further examining microbial dechlorination using this intimate data mining approach.

3.2 Methods

3.2.1 Analytes in PMF Analysis

Groundwater data regarding chlorinated ethenes measured in various aquifer systems (i.e., aquifers A, B, C, D, and E) was extracted from the Envista database. A description of the hydrogeology of the site is given in Chapter 1. The majority of the wells included in the investigation are monitoring wells screened at the water table or in the shallowest aquifers. Samples were collected between November 4, 2005, and September 9, 2011. Measured compounds of interest include tetrachloroethene (PCE), trichloroethene (TCE), 1,1-dichloroethene (1,1-DCE), *cis*-1,2 dichloroethene (*cis*DCE), *trans*-1,2 dichloroethene (*trans*DCE), as well as prospective breakdown products vinyl chloride (VC), ethene and ethane. The analytical methods reported for chemical measurements changed over time and different analytical methods were used in the early 1990s than those currently reported. A dataset containing samples measured using multiple sample preparation methods and instrumental techniques introduce challenges to applying factor analysis. In addition to varying detection limits, not all of the aforementioned analytes are measured

in each sample, which resulted in a heterogeneous dataset. There are many reasons why a different analytical method might be used. Changes in state regulations or in-house laboratory protocols, or the introduction of new instrumentation could trigger a change in analytical methods. In addition, samples have been measured at different laboratories using different methods throughout the years. In the 1990s ETC, Ponca City, and Enseco-East and Lancaster laboratories analyzed the groundwater samples. As of the late 1990s, Lancaster Laboratories and Environmental Chemistry Consulting Services have primarily analyzed groundwater samples.

Although heterogeneous data is difficult to work with, it is not impossible and applying PMF can still yield meaningful results. For example, factor analysis was applied to wastewater effluent and influent to investigate evidence of dechlorination of PCBs and PCDD/Fs.[28, 29] Concentrations of targeted PCB congeners were measured using method 1668A by various contract laboratories. This method allows the use of two possible gas chromatography columns, resulting in different congener coelution patterns within the dataset. Regardless, the PMF model was able to converge on solutions for the PCB dataset as well as a combined dataset of PCBs and PCDD/Fs samples.[28, 29]

3.2.2 Ethene/Ethane Analysis

Method 8015B outlines the analysis of volatile non-halogenated organic compounds, such as ethene and ethane, by gas chromatography separation coupled to flame ionization detection (GC/FID). No surrogate compounds are reported in method 8015B and the internal standards used in are 2-chloroacrylonitrile, hexafluoro-2-propanol, and

hexafluoro-2-methyl- 2-propanol.

3.2.3 Chlorinated Ethene Analysis

Chlorinated ethenes were analyzed using EPA method 8240, 8240A, and 624 between the years 1990 to 1995 and method 624 in 1993. Method 8240B was used between 1995 and 1998, when method 8260B started being applied in 1998 and continues to present day.

Chlorinated ethenes were measured via EPA methods 8240 and 8260, procedures used to analyze volatile organic compounds by gas chromatography/mass spectrometry (GC/MS) using purge and trap or direct injection technology. Method 8240 and 8260 are very similar and the procedures mainly differ in the chromatographic column used to separate analytes prior to detection. The methods can quantify most VOCs with boiling points below 200°C and the estimated quantification limit for both methods is 5 ug/L for groundwater samples.[30] EPA method 624 also outlines a procedure for VOC analysis by GC/MS using purge and trap technology. Sample preparation for Method 624 takes place in a specialized chamber, which differs from methods 8240 and 5030/8260. Samples included in the PMF analysis were predominantly prepared using method 5030B and analyzed by 8260B. Method 8260B designates the use of 4-bromofluorobenzene, 1,2-dichloroethane-d_4, and toluene-d_8 as surrogate standards in order to calculate the percent recovery of each analyte during the laboratory sample preparation and analysis. The following internal standards are used in order to quantify results: chlorobenzene-d_5, 1,2-dichlorobenzene-d_4, 1,4-difluorobenzene, fluorobenzene. It should be noted that these internal standards are aromatic organic compounds, unlike the chlorinated ethenes

which are aliphatic compounds. Analytes must have similar properties to their corresponding internal standard in order to make accurate determinations when using the internal standard method of quantification. This point is moot, however, since the surrogate recoveries were not available for analysis.

3.2.4 Ancillary Parameters

Ancillary parameters applied in correlations used to supplement PMF results include temperature (T, n = 57), pH (n = 57), redox (pE, n = 57), dissolved oxygen (DO, n = 57), alkalinity (ALK, n = 69), total organic carbon (TOC, n = 76), nitrite (NO_2^-, n = 44), sulfate (SO_4^{2-}, n = 75), sulfide (S^{2-}, (n = 35), methane (CH_4, n = 73), ferric iron (Fe^{3+}, n = 38), and ferrous iron (Fe^{2+}, n = 4). It should be noted that ferric iron and ferrous iron were not measured on a filtered sample, as indicated in the Envista database. Many other ancillary parameters were sometimes measured (sulfite, phosphate, total dissolved solids) but were not regularly measured along with the chlorinated ethenes and so could not be used for correlations. The fraction of aniline as the sum of aniline and nitrobenzene (%AN, n = 70) is also used here as an independent redox measurement and is further described in Chapter 1 and Chapter 2 (Section 1.3.2.1 and Section 2.2.3). These parameters can be used as indicators of the geochemical environment including redox state in the subsurface. Table 3-1 displays percentile concentrations (the Xth percentile concentration is that for which X% of the measured concentrations were lower) regarding each investigated measurement after preprocessing (trimming the dataset non-measured data and samples <50% BDL of all six analytes) the data matrix for PMF analysis. Analytical methods by which these ancillary parameters were measured are reported in

Chapter 1 (Section 1.3.2).

3.2.5 PMF Input Data Matrices of Chlorinated Ethenes

Groundwater data regarding chlorinated ethenes measured in various aquifer systems

(i.e., aquifers A, B, C, D, and E; see Section 1.2.1) was extracted from the Envista

database. The dates of the samples range from November 4, 2005 to September 9, 2011.

The vast majority of the water samples were extracted from monitoring wells screened

within the B aquifer. A total of 2,635 groundwater water samples were present in the

Envista database and only 465 samples quantified at least two of the seven CEs or

ethene+ane. Of these, 1,1-DCE was below detection limit (BDL) in more than half of the

samples and was therefore removed from the dataset. Measurements of 1,2-DCE (sum of

trans and *cis* isomers) were excluded from the dataset, because in most samples *trans*-

and *cis*-1,2-DCE were measured separately. Ethene was BDL in more than half of the

samples. The sum of ethene plus ethane was used as a single parameter since PCE can be

anaerobically dechlorinated to both ethene and ethane[31] and ethene is readily reduced

to ethane by bacteria. Including the sum of ethene plus ethane also provided a more

complete dataset for the analysis. Furthermore, more than 50% of the samples in the

initial dataset were below the detection limit for all analytes. After removing samples in

which the more than half of the targeted chloroethene analytes were not detected, as well

as analytes that were BDL in most samples, the final dataset consisted of 6 analytes

(Table 3-2) and 76 samples so that only 37% of the measurements were BDL. In

comparison, in Chapter 2, the chlorobenzene data set contained 6 analytes and 597

samples with only 12% of the measurements BDL. Also, in recent work by our research

group, less than 2% of the data was below detection in datasets on PCB congeners.[29, 32] As a result, concentration data ($X_{i,j}$) for 76 aqueous phase groundwater samples, measured between November 2005 and September 2011, were submitted to the PMF program. The PMF 2.0 software (YP-Tekniika KY Co., Helsinki, Finland) was used in this study.

For PMF2 analysis, three matrixes are submitted to the program: concentration, limits of detection (LOD), and uncertainty matrixes. For the concentration matrix, BDL values were replaced with a random number between zero and the method detection limit (MDL). No non-measured data were included in the dataset. The LOD matrix was assembled with the reported MDLs for each data point. The uncertainty matrix provides a means of decreasing the weight of missing and BDL data in the solution and it also accounts for measurement uncertainty.[33]   In addition, the uncertainty should account for temporal variability of the analytes during the monitoring period.[33] For the uncertainty matrix, a (x, 3x) matrix was used, [28, 32, 34-39], where x is the uncertainty assigned to all detected measurements of a given analyte and three times this value (3x) is assigned to all those non-measured data points or measurements BDL of that analyte.

The calculated relative standard deviation (RSD) of the surrogate recoveries is frequently used as x.[38, 39] Unfortunately, in this case surrogate recoveries were not available to estimate the uncertainty matrix. Instead, we assigned an uncertainty value to each compound using our best judgment after reviewing the available information regarding the analytical method and after considering each compound's physical-chemical

properties and their implications during field sampling activities. PMF2 model
uncertainty assignments for each investigated CE are presented in Table 3-3. PCE and
TCE were assigned a base (x) uncertainty value of 0.18. *Cis*-DCE, *trans*-DCE, and VC
were assigned a base uncertainty of 0.1. Additionally, the sum of ethene and ethane
(ethene+ane) was assigned a base uncertainty of 0.4. Again, all measurements below
detection limit (BDL) were assigned three times the aforementioned values for each
respective analyte. A higher uncertainty was assigned to ethene+ane to down-weight the
influences arising from sample volatilization and to account for the reactivity of ethene
and ethane in the subsurface. PCE and TCE given a higher uncertainty assignment than
DCE and VC due to higher affinity to undergo sorption and dechlorination in the
subsurface. There is not a large range between these uncertainty assignments and, for the
most part, more volatile and/or reactive compounds are assigned a slightly higher
uncertainty. Lastly, the robust mode was used in this study to reduce the influence of
extreme values on the PMF solution by down-weighting very high concentrations.

3.2.6 Spatial Trends

The ArcGIS software (version 10.2.2) was used to visualize trends of the factor solutions
throughout the various wells and dates considered in the study (Figure 3-3). The
coordinate system was defined for the layer file using datum GCS _NAD_1983
(geographical coordinate system_North American datum_1983) file. The layer file was
then exported as a shape file.

3.2.7 Correlation Analysis

The columns in the G matrix are called 'factors' and each row in the G matrix represents the strength of each sample in the dataset. The concentration (i.e. the strength) of each factor in each sample (i.e., G-matrix) was correlated with measurements of ancillary parameters such as DO, pH, and nutrients to identify locations where microbial dechlorination is occurring in the subsurface using Spearman's correlations.

$$\rho = 1 - (6 \Sigma \, d_i^2 / n(n^2 - 1))$$ (Eqn. 3-1)

Spearman's correlation coefficient, ρ, is defined as the Pearson's correlation coefficient between two ranked variables where, n is equal to the sample size and d is the difference in rank between two ranked variables. It is a non-parametric statistical analysis well suited to the dataset. Spearman correlations have been applied to assess surface water[40] as well as groundwater[41-43] quality data. The method makes no assumptions about the distribution of the data and is more appropriate for datasets with large outliers, which could otherwise mask meaningful relationships between variables. For these correlations, the samples were ranked two ways: first by the absolute concentration of each factor, and second by the relative contribution of each factor to each sample (i.e. the factor concentration in a single sample was divided by the sum of all of the factors for the sample and this percentage was ranked).

3.3 Results

3.3.1 Description of Dataset

The 10th, 50th, and 90th percentile (the Xth percentile concentration is that for which X% of the measured concentrations were lower) concentrations of the investigated

analytes as well as the ancillary parameters are reported in Table 3-1 for datasets after preprocessing for PMF analysis. Chlorinated ethene (CE) concentrations are highest in the southern portion of the site (Figure 3-1). Elevated concentrations of the contaminants are observed in the Fluoroproducts area (AOC #1) located in the southwestern portion of the site adjacent to the Delaware River, as well as the southernmost portion of the site along the Salem Canal. Ethene is present at highest concentrations in the southwestern portion, whereas ethane has elevated concentrations throughout the entire southern half of the site. Given that ethene is reduced to ethane under anoxic conditions [31] and ethane may be oxidized to ethene under oxic conditions, this may imply that the groundwater in the southern portion of the site is under more highly reducing conditions. NJ Class IIA groundwater quality criteria for PCE, TCE, *cis*DCE and *trans*DCE, and VC are 0.4 µg/L, 1 µg/L, 70 µg/L, 100 µg/L, and 0.08 µg/L respectively. Concentrations of PCE, TCE, *cis*DCE and *trans*DCE in the groundwater samples considered in the study range from 0.9 to 3,500 µg/L, 1 to 1,700 µg/L, 1 to 2,300 to µg/L and 0.9 to 21 µg/L, respectively. Lastly, the concentrations of vinyl chloride and the sum of ethene and ethane (ethene+ane) ranged from 1 to 260 µg/L and 1.1 to 10,095 µg/L, respectively. The median detection limit for the compounds was 1.0 µg/L. The least frequently detected compounds in the PMF data matrix are *trans*DCE and VC, which are BDL in 72% and 46% of the samples, respectively.

3.3.2 Correlations with Raw Analyte Data

Spearman's rank-order correlations were performed in attempt to identify trends between ancillary measurements and analyte concentrations. When considering absolute

measured concentration (ppb) data, (Table 3-4) alkalinity correlated positively with

*trans*DCE, VC and ethene+ane. Since alkalinity is produced by anaerobic microbial

activity[44], its correlation with these analytes suggests that they are products of

biodegradation. This is in agreement with the current understanding of the pathways of

CE degradation reviewed above. Similarly, ferrous iron is correlated positively with

*cis*DCE, VC, and ethene+ane. This may indicate that reduction of CEs is occurring under

iron-reducing conditions. Methane is correlated positively with TCE, *cis*DCE,

*trans*DCE, VC, ethene+ane and methane is not correlated with the parent compound

(PCE), possibly indicating that CE reduction is occurring under methanogenic conditions

as well. Sulfate is correlated positively with *cis* and *trans*DCE and TOC is correlated

positively with all investigated chloroethenes. It should be noted that raw (absolute)

concentrations of ferric iron, ferrous iron, and methane are not correlated with each other.

The percent of TOC attributed to the compounds under investigation in the dataset range

from 0.03% to 32.1% with average and median values of 3.0% and 0.6%, respectively.

Thus the correlation between TOC and the analytes is not due to the analytes comprising

a large proportion of TOC. Rather, the correlation probably arises from the sorption of

the analytes on the TOC or it may be comprised of other analytes other than the

chlorinated ethenes explored here. pH is correlated negatively with PCE and TCE. It is

interesting that alkalinity is positively correlated with breakdown products (DCE, VC,

and ethene+ane) and the parent compounds (PCE and TCE) are negatively correlated

with pH. These results are consistent with the reductive dechlorination process.

In contrast with the absolute concentrations described above, correlations performed on normalized concentrations (Table 3-4) show less consistency in terms of CE degradation. Correlations performed on normalized concentration data show alkalinity is correlated negatively with *trans*DCE and positively with ethene+ane. Ferrous iron is correlated positively with PCE and *trans*DCE and ferric iron is correlated positively with ethene+ane. Methane is correlated negatively with PCE and *trans*DCE and nitrite is correlated positively with PCE. In addition, sulfate is correlated negatively with PCE and positively with *cis*DCE. pH is correlated positively with ethene+ane, whereas the oxidation-reduction potential is correlated negatively. Lastly, TOC is correlated positively with TCE and negatively with *cis* and *trans*DCE and VC. Whereas the correlations with ranked concentrations (above) made sense in terms of CE degradation products being correlated with ancillary parameters indicative of microbial activity, these correlations with the normalized analyte concentrations tell a less coherent story of CE degradation. Correlating the raw analyte concentration data with ancillary measurements can therefore be misleading.

3.3.3 PMF Analysis

PMF was run requesting 2 to 6 factors. The PMF model was run starting at 10 different initialization points (seed values) for each requested number of factors. Determining the 'correct' number of factors is a major task of factor analysis. Here, the 3-factor solution was selected for the following six reasons outlined below.

- First, to ensure that all factors contributed positively and significantly to the measured sum of the analytes, the G-matrix (mass contribution) was regressed

against the sum of the analytes. This regression for the 3-factor solution showed all factors with positive and significant ($p < 0.05$) coefficients.

- Second, the model results are stable and reproducible. The RSD of the G and F matrixes are commonly used an indicator of model stability.[29, 32, 38, 39] Here we chose the highest number of factors that provide a stable model solution (Table 3-5). The average RSD of the G and F matrixes for all 10 seed runs in the 3-factor model are 0.2% and 0.9%, respectively. When another factor is requested, the average RSD of the G matrix jumped to 61.6%, which indicates too many factors had been requested. These results demonstrate that the quality of the data is sufficient that PMF analysis can be performed and can yield stable model solutions, which addresses the first objective mentioned above.

- Third, the resolved factors are independent. Plots of the G-matrix of one factor versus the G-matrix of another factor and can be used to assess rotational ambiguity[45] and ensure that the factors are not correlated, i.e. they are independent of each other. The G-space plots indicate that each factor is independent of the others and rotation of the data matrix is not necessary (Figure 3-4).

- Fourth, plots of modeled versus measured concentrations are in good agreement. The chosen number of factors must provide a good fit (correlation) between the measured concentrations and the modeled analyte concentrations. The overall agreement between the measured and modeled concentrations increase in comparison to the 2-factor model. The 3-factor model yielded an R^2 value better than 0.99 for three out of the six analytes included in the data matrix (Table 3-6).

For the remaining two analytes, the R^2 values improved to greater than 0.85 after removing outlier data points (n = 7 for PCE and n = 4 VC out of 76 samples). The inclusion of very high or very low concentrations can result in outliers. Since data points BDL are replaced with a random number between zero and the detection limit, outliers usually a result of low concentrations. Elevated concentrations may also be outliers due to the model operating in robust mode, which down-weights very high concentrations.

- The fifth criterion for determining the correct number of factors is that the model results have physical meaning. The fact that PMF resolved factors resembling stages of dechlorination is a good indicator that results are physically meaningful. In addition, too many factors should not be requested for this data matrix because the dataset is relatively small and contains few analytes. For example, it would not make sense to accept a 5-factor solution when there are only 5 analytes included in the model.

- The sixth and final criterion for determining the correct number of factors is that results from analyzing variations of the input matrices with PMF are in agreement with those presented. Variations of the chlorinated ethene dataset were investigated where groundwater samples taken within 90 days of each other were date-matched to fill in missing data in effort to obtain a more complete dataset. The output results from date-matched PMF runs are virtually identical to the results reported here. In addition, investigations of the dataset suggest that ethene+ane is important to the solution, since excluding these analyte(s) dramatically change the PMF solution. Moreover, results also suggest *trans*DCE

is not important to the PMF solution, as excluding it from the model does not

change the solution noticeably.

3.3.4 Source Profiles

The PMF model resolved three sources profiles (factors) in the monitoring dataset of

chlorinated ethenes (Figure 3-5). Factor 1 is comprised of nearly 100% ethene+ane and

constitutes approximately 67% of the total mass in the dataset (Figure 3-6). Because

ethane+ane are known to be dechlorination products of VC and *cis*DCE, we conclude that

factor 1 represents an advanced CE dechlorination signal. The factor also contains 7.5%

of the *trans*DCE mass and 2.5% of the VC mass in the dataset. The fact that ethene+ane

appear in the different factor than most of the DCE and VC mass suggests that they either

come from a different dechlorination process (perhaps a more advanced stage of

dechlorination) or that they experience different fate/transport in the subsurface. This

could occur because ethane and ethane are more volatile than the DCE isomers and VC,

or because they more readily undergo aerobic biodegradation than the CEs.

Factor 2 is comprised of 86% *cis*DCE, 10% VC and 3% TCE and constitutes 16% of the

total mass of the solution. This factor contains over 99% of the measured *cis*DCE mass

and 96% of the VC mass. Because *cis*DCE is known to be a product of PCE and TCE

dechlorination, we conclude that Factor 2 represents a partial CE dechlorination signal.

Factor 2 also contains 56.0% of the measured *trans*DCE and 3.3% of TCE. The fact that

cis and *trans* DCE as well as VC appear together in this factor indicates that they either

arise from the same process or are transported together from the same location. Since

transport in general is limited in the subsurface, it is more likely that *cis* and *trans* DCE

and VC arise from the same dechlorination process. In factor 2, the ratio of the total

mass of *cis*DCE to *trans*DCE in the solution is 183 and the ratio of *cis*DCE to VC is 8,

whereas the ratio of *trans*DCE to VC is 0.05. Although *cis*DCE is the typical biotic

product of CE dechlorination, small amounts of *trans*DCE can be produced.[46] If use of

*cis*DCE or VC on the site were important sources of these chemicals, we would expect

them to appear in by themselves in separate factors, perhaps in addition to a

dechlorination factor containing both. The fact that they do not suggests dechlorination is

responsible for the vast majority of the *cis*DCE and VC detected at the site. This

conclusion is consistent with the current understanding of CE degradation pathways in

groundwater summarized above.[2-4, 17, 47]

Finally, factor 3 comprises 17% of the total mass of the dataset and is composed of a ~1:4

ratio of PCE and TCE. It comprises virtually 100% of the PCE mass in the data set,

96.6% of TCE and 36.6% of *trans*DCE. Based on the historic use of PCE and TCE at the

site, we conclude that factor 3 represents a source term. If correct, this suggests that the

main source of TCE on site is historical usage of TCE, not dechlorination of PCE. The

production of TCE from PCE is necessary for the further production of DCE isomers and

VC. The results may suggest that any TCE formed is rapidly reduced to dehchlorination

products (DCE and VC) under reducing conditions. Therefore high concentrations of

factor 3 would be expected only in areas where the redox potential is relatively high and

little or no reductive dechlorination is occurring. This may also occur where the redox

potential is low and the threshold concentration of the parent compound is not sufficient
for reductive dechlorination.

In order to determine whether the factors are indicative of physical processes (i.e.
preferential transport), it is helpful to consider the octanol-water partition coefficient
(K_{ow}) and the Henry's law constant (K_H) of each analyte (Table 3-2). K_{ow} is an indicator
of the hydrophobicity of a chemical compound, and is defined as the ratio of the
concentration of a chemical in *n*-octanol and water at equilibrium conditions and a
specified temperature.[48] The value provides insight to how readily a chemical
compound would partition out of the aqueous phase and onto organic material such as
aquifer solids, biomass, or even DNAPL. In addition, K_H is a measurement of the
equilibrium partitioning between air and water at a specified temperature and indicates
how readily a chemical compound would partition out of the aqueous phase and into the
air.[48] If the concentrations of the investigated analytes were primarily controlled by
physico-chemical properties and the chromatography effect (i.e. more rapid movement
through groundwater of less hydrophobic chemicals), *cis*DCE would be found in the
same factor as *trans*DCE. Moreover, PCE and TCE would not end up in the same
factors.

The PMF results suggest factors 1 and 2 are a product of microbial degradation processes
rather than a product of their physical-chemical properties. The fact that these patterns
are observed and the PMF results are interpretable and tell a coherent story about the fate

of CEs in the subsurface suggests that PMF is a useful tool for analyzing groundwater data. These results address the second objective, goal B, of the work.

3.3.5 Temporal and Spatial Trends in PMF Factors

A total of 41 wells had enough data to assess spatial distribution of the chlorinated ethene solution (Figure 3-3). 'Hot spots' of the relative and absolute concentrations of the factors are spread out across the site, with some grouping occurring near the perimeter and a canal area (Figure 3-7 and 3-8). Monitoring wells M12-M02B and M12-M01B are high in the source factor and low in both the degradation factors. These wells are located in the center of the site and both are screened in the B aquifer and have elevated concentrations of TCE. The following geochemical measurements were reported in June 2011 for monitoring well M12-M02B: ferric iron = 1,500 μ g/L, sulfate = 93,200 μ g/L, sulfide = 430 μ g/L, methane = 290 μ g/L, TOC = 666,000 μ g/L, and alkalinity = 455,000 μ g/L. In addition, wells D08-M01A, G08-R01C and G08-R01D are high in the source and partial degradation but low in advanced degradation factor. Monitoring well D08-M01A is located in the southwestern corner of the site adjacent to the Delaware River and screened in the A aquifer, which is a shallow unconfined aquifer system. Low concentration of methane (550 μ g/L) was reported in well D08-M01A in November 2011.

Wells G08-R01C and G08-R01D are located in the southern portion of the site and are characterized as recovery wells and screened in confined aquifer systems at greater depths (i.e., C and D aquifers) and are targeted at the source of contaminants (mainly

DNAPL but also aqueous phase contaminants); they are dominated by the source term. Low concentrations of methane were measured during July 2009 in wells G08-R01C (100 μ g/L on July 9, 2009; 170 μ g/L on July 21, 2009, and 150 on July 28, 2009) and G08-R01D (220 μ g/L on July 9, 2009 and 62 μ g/L on July 28, 2009). Alkalinity concentrations during July 2009 in wells G08-R01D is as follows: 50,200 μ g/L on July 9, 2009 and 43,200 μ g/L on July 28, 2009. Alkalinity concentrations during July 2009 in well G08-R01C is as follows: 112,000 μ g/L on July 21, 2009 and 100,000 μ g/L on July 28, 2009.

Conversely, monitoring wells G05-M06B and H06-M01C, which are located adjacent to the Salem Canal and are screened in the B and C aquifer, respectively are high in the advanced and partial degradation factors and low in the source term. This could indicate complete dechlorination of chlorinated ethenes to the relatively innocuous ethene and ethane can occur in these wells. High concentrations of methane were measured in G05-M06B (4,500 μ g/L in March 2010, 5,000 μ g/L in March 2011, and 5,900 in September 2011) and in H06-M01C (7,000 μ g/L in March 2009, 9,600 μ g/L in October 2009, 8,100 μ g/L in June 2010, 5,700 μ g/L in October 2010, 5,900 in March 2011, and 5,300 μ g/L in September 2011).

In addition, the advanced degradation factor is high and both the partial and source factors are low in wells D11-M01B, H13-M01A, H13-P01B, H16-M01B, and O12-M03B. Monitoring wells D11-M01B and H16-M01B are both screened in the B aquifer

and located adjacent to the Delaware River, however D11-M01B is located in the southwestern portion of the site and H16-M01B is located in the northwest portion of the site. In June 2011, the following ancillary data were measured in well D11-M01B: ferric iron= 119,000 μ g/L, ferrous iron = 102,000 μ g/L, sulfate = 3,900 μ g/L, sulfide = 4,400 μ g/L, methane = 8,100 μ g/L, TOC = 85,800 μ g/L, and alkalinity = 400,000 μ g/L. The following ancillary data is available for well H16-M01B in June 2011: ferric iron = 39,200 μ g/L, ferrous iron = 63,100 μ g/L, methane = 7,600 μ g/L, sulfate = 1,150,000 μ g/L, sulfide = 19,400 μ g/L, TOC = 72,900 μ g/L, alkalinity = 1,240,000 μ g/L, and pH = 6.31.

Wells H13-M01A and H13-M01P are found in the center of the site. H13-M01P is continuously pumped from the subsurface in order to control offsite migration of groundwater contaminant plumes. Monitoring well 012-M03B is located in the eastern, central portion of the site and also screened in the B aquifer. Limited ancillary data is available for H13-M01A, H13-M01P, and O12-M03B but these wells do have elevated concentrations of ethene+ane, which could indicate complete dechlorination of CEs has occurred. Alternatively, it is possible that ethene and ethane is these wells are produced by some other process or source. Ethene+ane could be products of other reactions involving chlorinated ethanes, which are used onsite. Also, ethane is widely used in petrochemical manufacturing to produce ethene, which appears on the Chambers works facility's Toxic Release Inventory (TRI) report.[49]

   In summary, well locations high in degradation factors (factor 1 and factor 2) are either

located near the perimeter of the site or in close proximity to pumping or collection wells.

Areas high in the source factor (factor 3) are spread out across the site. This could be

explained by the increased dispersion (mixing) in the system due to increased flow in the

subsurface. More mixing in the system could promote reductive dechlorination by

making one or more components of the reaction readily available to the responsible

dechlorinators. Another possibility is attributed to the fact that dechlorination products

consist of analytes that are generally more mobile in the aqueous phase then the parents

which could account for their greater abundance at these well points.

The following discussed have at least 5 sample measurements and are located adjacent to

the Salem Canal. Temporal trends of the absolute and relative concentrations of the G-

matrix of each factor were assessed in wells with enough data (> 5 sampling dates)

(Figure 3-9). The trends suggest that dechlorination conditions differ not only by well

location but also by time within locations, which addresses goal C of the work. This is

not surprising since there is large temporal (as well as spatial) heterogeneity of CE

dechlorination in groundwater systems.[3-5, 20] From March 2009 to September 2010,

the source term appears to be increasing in well I05-M02B, while the partial and

advanced degradation factors are smaller and fluctuate slightly throughout time.

Inhibitory effects of either too high or low parent compound (PCE or TCE) concentration

could explain wells with high source factor and low in degradation factors. Degradation

may not be occurring in wells due to a low total concentration of parent compounds,

which is not high enough to promote dechlorination. Some have suggested that there is a

minimum concentrations of electron acceptor for reductive dechlorination of CEs to occur (total VOC > 50 μg/L).[50]   Conversely, very elevated concentrations of the parent compounds can be toxic to certain microorganisms responsible for dechlorination. Chlorinated ethene concentrations exceeding approximately 700 μM have shown to inhibit reductive dechlorination.[20] Other important factors for reductive dechlorination include favorable temperature (T > 10C or T < 45C) and pH (pH<5.5 or pH > 9) as well as the bioavailability of nutrients and absence abiotic and biotic inhibitors.

In conclusion, the data indicates spatial and temporal heterogeneity of dechlorination activity throughout the site. The advanced dechlorination factor is increasing and the source and partial dechlorination factors are decreasing in monitoring well O12-M03B, H13-M01A/B, H13-P01B, D11-M01B, and H16- M01B/C. This could indicate complete or late stage CE dechlorination. Well D11-M01B and H16- M01 B/C are located adjacent the Delaware River.

The partial and advanced dechlorination factors are increasing as the source factor is decreasing in monitoring wells H06-M01C and G05-M06B which may be characterized as a middle stage of CE dehclorination. Wells H06-M01C and G05-M06B are located along the Salem Canal. In addition, the source and partial dechlorination factors are increasing and the advanced dehclorination factor is decreasing in wells D08-M01A, G08-R01C and G08-R01D. Incomplete dechlorination (known as "cisDCE/VC stall") is observed in shallow-aquifer monitoring well D08-M01A, as wells as recovery wells G08-R01C and G08-R01D. The presence of chemical inhibitors may inhibit dechlorination in

recovery wells and influxes of oxygen in shallow aquifers may cause an insufficient reducing environment to sustain CE dechlorination.[50] Lastly, the source factor is increasing while both degradation factors are decreasing in wells M12-M01B, M12-M02B and the following wells located along the Salem Canal area: H06-M02B, I05-M02B, F05-M02B, and G04-M02B. Complete dechlorination does not seem to occur in the aforementioned wells as the advanced dechlorination factor is consistently decreasing and the source factor is either increasing or static.

3.3.6 Spatial Trends of Ancillary Measurements

Spatial distribution of the raw ancillary measurements was examined using ArcGIS software. The raw concentration gradients of ancillary parameters were plotted throughout the wells considered in the study and observations regarding select redox indicators and nutrients are presented below.

- Ferrous & ferric iron: Concentrations of ferrous iron over 100 ppm are present in wells that are high in factor 2 (partial degradation) such as D11-M01B, H10-M02C, and K11-M01B showing. Concentrations around 50 ppm of ferrous iron are also found in well H06-M02B and H06-M01C, which are high in factor 2 (partial degradation). Well F05-M02B is high in factor 1 (advanced degradation) and also shows concentrations greater than 100 ppm of both ferrous iron and ferric iron (Figure 3-10).

- Sulfate & sulfide: The highest concentration of sulfide (19,400 μg/L) was measured in H16-M02B, which is also high in factor 1 (advanced degradation).

For the dataset considered, sulfate concentration range between 1.5 to 3,710 mg/L with a median value of 146.5 ppm. Spatial trends suggest areas where factor 2 (partial degradation) is high are in the same areas with high concentrations of sulfate, which is defined here as any concentration exceeding the 50th percentile concentration of the sulfate data (> 147 ppm). Wells H06-M01C and H06-M02B are high in factor 2 (partial degradation) and sulfate concentration ranges between 148 ppm to 278 ppm. Areas that are high in the factor 1 (advanced degradation) are low in sulfate concentration. Wells F05-M02B, F11-M01B, G04-M02B and G05-M06B show low sulfate concentrations between 19 and 76 ppm and are high in the factor 1 (advanced degradation). It should be noted that areas with very elevated concentrations of sulfate (exceeding the 90th percentile concentration of 627 ppm sulfate) are low in both factor 1 and factor 2 (advanced and partial degradation factors, respectively) and high in factor 3 (source). Wells G14-M01B, G15-M01B, and M10-M01B are high in factor 3 (source) and contain very high sulfate concentrations of 3,710 ppm, 1,880 ppm, and 1,180 ppm, respectively (Figure 3-11). This may suggest a sulfate threshold for the responsible dechlorinating microbial community.[24, 51] It could be that high parent compound concentrations are toxic to sulfate reducers and dechlorinators alike, however a recent study in 2013 by Garcia-Solares *et*. *al*. [52] shown that sulfate reducing activity was not inhibited in enriched sediments amended with 200 to 900 µg/L TCE. Some anaerobic systems partially dechlorinate PCE, whereas others achieve complete dechlorination. As previously stated, many microorganisms (including sulfate reducers) can dechlorinate PCE to DCE or VC,

but very few can further dechlorinate DCE or VC to ethene or ethane. It is common to see a stall in CE dechlorination under sulfate-reducing conditions and complete dechlorination under methanogenic condition in both laboratory and field conditions.[53] An alternate explanation for the stall in CE dechlorination is the presence of one or more co-contaminants (such as chloroform [54] [50]), which is inhibiting reductive dechlorination in the abovementioned wells. In June 2011, carbon tetrachloride, chloroform, and dichloromethane groundwater aqueous phase concentrations were 26,000 µg/L, 22,000 µg/L, and 9,600 µg/L, respectively.

- Methane: High concentrations of methane (exceeding the 50th percentile concentration of 2,100 µg/L methane) are mostly located in areas that are high in the factor 1 (advanced degradation) such as the following wells: D11-M01b, F05-M02B, H06-M01B, H16-M01B, G05-M06B, and Q09-M01B. Methane concentrations as high as 11,000 µg/L (June 2010) are detected in well I05-M02B, where factor 3 (source) is prominent (Figure 3-12). These results are also consistent with the idea that complete CE dechlorination is achieved under methanogenic conditions.

- Alkalinity and TOC: High concentrations of alkalinity (exceeding the 50th percentile concentration of 116,000 µg/L ALK) are also present in wells that are high in factor 1 (advanced degradation) such as wells D11-M01B, G05-M06B, H16-M01B, K11-M01B, K12-M01B, and 012-M01B (Figure 3-11). Dechlorination can depress the pH of the system.[55] Both pH and alkalinity

(between 10,200 and 77,200 µg/L) is low in the abovementioned wells where pH

is between 4.9 and 6.6.

- In addition, total organic carbon (TOC) concentrations are lower in areas where

  factor 2 (partial degradation) is high such as wells G08-R01C, G08-R01D, K08-

  M01C, K08-M01D, and K12-M01B (Figure 3-12). This may be because factor 2

  correlates with sulfate reduction. Spearman correlation performed on TOC with

  sulfate and sulfide reveal a positive correlation between TOC and sulfide (n= 35,

  p = 0.001) and no correlation between TOC and sulfate (n = 75, p = 0.238).

  Organic matter acts as an electron donor and thus a redox partner for electron

  acceptors during microbial metabolism. Dechlorination needs an electron donor

  and some of the TOC can serve as an electron donor to drive the dechlorination

  reaction. The concentration and bioavailability of organic matter (plus salinity

  and sulfate concentration) have been found to be important factors in controlling

  the rate of sulfate reduction and dechlorination.[56] Elevated TOC concentrations

  (exceeding the 90th percentile concentration of 96,160 µg/L TOC) are present in

  areas with that are also high in factor 3 (source) in wells M12-M01B, M12-

  M02B, and M12-M03B.

3.3.7 Correlation Analysis

Spearman's rank-order correlations were performed in attempt to identify ancillary

parameters that are correlated with PMF factors 1 and 2, which are indicative of

dechlorination. When correlations are performed on the ranked absolute concentration

data (Table 3-7), the advanced degradation factor (factor 1, ethene + ethane) is correlated

positively with alkalinity, ferrous iron, ferric iron, methane and TOC. The partial

degradation factor (factor 2, *cis*DCE and VC) is correlated positively with ferrous iron

and sulfate. In addition, the source factor (factor 3, PCE + TCE) is correlated positively

with methane, TOC, and negatively correlated with pH. These correlation results are

concurrent with observations from concentration plots of ancillary parameters with

respect to factor placement (Figures 3-10, 3-11, 3-12).   In Figure 3-11, the well locations

with high sulfate concentrations are high in partial degradation (factor 2) and locations

high in alkalinity are high in advanced degradation (factor 1). Results from the

correlation analysis confirm a positive correlation between partial degradation (factor 2)

and sulfate and advanced degradation (factor 1) and alkalinity.

Correlations were also performed on the *relative* contribution of each factor to each

sample. When the correlations are performed on normalized concentration data of the

model output (Table 3-7), the advanced dechlorination signal is correlated positively with

alkalinity, ferrous iron and pH and is correlated negatively with sulfate and redox. In

contrast, the partial degradation signal is correlated positively with sulfate and negatively

with TOC. Finally, the source term is correlated negatively with alkalinity and pH and it

is positively correlated with TOC and redox. Those correlations in agreement with

correlations performed on ranked absolute concentration data include the positive

correlation between the advanced degradation signal and alkalinity and ferric iron as well

as the positive correlation between sulfate and the partial degradation signal. The source

term also has multiple agreements including the negative correlation with pH and the

positive correlation with TOC. A compilation of correlation results between model output and certain ancillary parameters are displayed in Table 3-8 and Table 3-9.

PMF has proven a useful tool for elucidating patterns within the monitoring dataset that would otherwise have been overlooked by only investigating the raw analyte concentration dataset. Differences that arise between correlations performed on model output and measured analyte concentrations are attributed to PMF essentially smoothing the dataset by eliminating some high concentration outliers The main difference between using absolute and normalized concentration data in PMF is that correlations of ancillary data with model output using the absolute concentration data do not reveal a distinction between what happens under methanogenic conditions. Specifically, both the partial and advanced dechlorination products are correlated with methane (Table 3-9). Correlations performed on *relative* concentrations of model output are more useful for interpretation.

3.4 Discussion

Three factors were resolved in the chlorinated ethene groundwater dataset. Correlations performed on model output of both absolute (Table 3-8) and *relative* (Table 3-9) concentrations of each PMF factor and ancillary parameter reveal relationships between CE dechlorination pathway and redox conditions. Factor 1 represents an advanced stage of dechlorination and correlation results with model output using absolute concentrations as input reveal a positive relationship with ferric and ferrous iron, alkalinity, methane and TOC. Correlations results with *relative* concentrations of model

output reveal a positive relationship between factor 1 and alkalinity, ferric iron, and pH and a negative relationship with oxidation-reduction potential (redox, Eh) and sulfate.

An oxidation-reduction potential < -100 mV is generally required for organohalide-respiring bacteria. [43, 50] Studies have shown reductive dechlorination of DCE occurs under both methanogenic and sulfate-reducing conditions [12, 22, 26], while dechlorination of VC occurs, for the most part, under methanogenic conditions [31, 54, 57, 58]. Studies have also shown abiotic dechlorination of higher chlorinated CEs to ethene and ethane under iron-reducing[9-11] conditions. Results from the correlation analysis on *relative* concentration on model output reveal a negative correlation between advanced dechlorination and redox and sulfate. Furthermore, results from the correlation analysis with model output using absolute concentrations as input show a positive correlation between methane and the advanced dechlorination factor. Finally, advanced dechlorination is positively correlated with TOC, which could be explained by the factor's negative correlation with sulfate, assuming TOC is a good indicator of the dissolved organic matter in the system. It should be noted that TOC was not measured on filtered samples and TOC does not correlate with field specific conductance (n = 57) or field turbidity (n = 22). Sulfate reduction and dechlorination will more readily occur when there is enough bioavailable organic carbon in the system.[24] It is intuitive that the total sulfate concentration in the system is a controlling factor of sulfate reduction. Furthermore, TOC serves as an electron donor for dechlorination and thus drives the dechlorination reaction. In order for redox reactions to proceed, there is a required threshold concentration for the electron donor and/or electron acceptor. For example,

sulfate concentrations > 1,000 mg/L and TOC concentrations < 20 mg/L may limit reductive dechlorination activity because sulfate-reducers may outcompete dechlorinators under such conditions.[43, 50] On the other hand, when the total sulfate concentration is low in a reducing environment, microorganisms will seek out another available electron acceptor in the system.

The positive correlation between the advanced dechlorination factor (factor 1) and ferric iron could be explained by the manner in which the aqueous groundwater samples were measured for iron. Iron could be present as many different species and complexes in the subsurface depending on redox and pH conditions. Iron could be present as the soluble ferrous iron ion or insoluble iron (III) hydroxide in an aquifer (Figure 3-13), not to mention other complexes with organic or inorganic species. The positive correlation between the advanced dechlorination factor and ferric iron could be attributed to the factor's positive correlation with alkalinity and pH and thus an artifact of either sample collection and/or laboratory measurement. This could account for the presence of ferric iron in the samples since ~80% of the groundwater samples in the investigated CE dataset were not filtered before analysis. Moreover, in order to confirm the occurrences of other degradation processes, dichloroacetylene, chloroacetylene and acetylene measurements would be needed.

Factor 2 represents a partial dechlorination signal of higher chlorinated ethenes to *cis*-DCE and VC. Both sets of correlation results of factor 2 (absolute and *relative* concentrations) and sulfate reveal a positive relationship. In addition, correlations

between absolute concentrations of factor 2 and ferrous iron show a positive

relationship. While reductive dechlorination of *cis*DCE to VC is typically only observed

under the strongly reducing conditions typical of methanogensis, partial dechlorination of

PCE and TCE to *cis*DCE can occur under iron reducing and sulfate reducing

conditions.[59] This may indicate that a less extreme dechlorination regime is producing

the DCE isomers and VC in the subsurface onsite. Finally, the negative correlation

between *relative* concentrations of the partial degradation factor and TOC could be

attributed to the fact that more sulfate reduction is occurring as explained above.

The last source profile, factor 3, represents a source of higher-chlorinated ethene parent

compounds, PCE and TCE. The fact that factor 3 is correlated positively with redox

(correlations with *relative* concentrations) and negatively with pH (correlations with

absolute and *relative* concentrations) makes sense. PCE and TCE will not be subjected to

reductive dechlorination in less reducing (more oxidizing) environments. Additionally,

aqueous phase TCE and PCE solubility increases with decreasing pH[60], so more mass

will partition to aqueous phase in environments with lower pH. What is interesting is the

positive correlation between absolute concentrations of the source term (factor 3) and

methane. Dehalorespiration is more energetically favorable than methanogenesis. There

might be threshold phenomena here for further PCE and TCE dechlorination. Although

methanogenesis generates alkalinity, acidification during fermentation of added electron

donors can occur and inhibit reductive dechlorination. Unfavorable pH ranges for

reductive dechlorination is pH < 5.5 or > 9.[43, 50] Correlations also reveal a negative

relationship between *relative* concentrations of the source term and alkalinity, indicating

less microbial dechlorination is occurring where the source term is high. The fact that the source term is both negatively correlated with pH and alkalinity may be explained by a buffer effect. As per Eqn. 3-2, the total alkalinity measurement quantifies various alkaline species in the groundwater sample, one of which could be consumed by another process taking place.

$$ALK_{Total} = [OH^-] + [HCO_3^-] + 2[*CO_3^{2-}] + [HPO_4^{2-}] + [H_3SiO_4^-] + [HS^-] - [H^+] \quad \text{(Eqn. 3-2)}$$

For example, bicarbonate, HCO_3^-, is the dominant carbonate species under environmentally relevant pH conditions and it is consumed and produced by many microorganisms during metabolic processes such as acetogenesis and methanogenesis, both of which generate bicarbonate.[61] Thus the disparity between the pH and alkalinity trends for factor 3 could be explained by the positive correlation between absolute concentrations of factor 3 and methane. Lastly, as shown by correlations on both absolute and *relative* concentrations of factor 3, the source term is also positively correlated with TOC. The wells elevated in factor 3 include those with the highest fractions of the TOC attributed to the measured chlorinated ethenes themselves, which may suggest a sorption phenomenon is occurring in the samples. A total of 28% of the measured TOC in the groundwater sample extracted from monitoring well D15-M01C in November 2008 was attributed to the measured chlorinated ethenes themselves (total chlorinated ethenes / total organic carbon = %CEs). Here, PCE concentration was elevated and measured at 3,100 ppb. In monitoring well G15-M01B 16% of the measured TOC in the groundwater sample collected in June 2011 was also attributed to

PCE in this sample (3,500 ppb). It is unlikely the high concentrations of PCE in the samples are proving toxic to dechlorinators since PCE dechlorination has been shown to occur near saturation concentration (> 0.9 mM).[62] In addition, elevated concentrations of PCE are more inhibitory to methanogens than dechlorinators.[62] The fact the PMF output reveals a rational and cohesive story of microbial dechlorination in the subsurface, addresses goal D of the work.

An alternate data mining approach has been recently used by Lee *et al*. for a dataset containing 10 separate hazardous waste sites monitored for ~3 month period for chlorinated ethene concentrations, geochemical data, and gene copies of *Dehalococcoides* (*Dhc* 16S rRNA).[43] The classification and regression tree (CART) algorithm was assembled and three classes of CE-dechlorination potential were assigned based on the amount of ethene, VC, or PCE/TCE in a sample.[43] Results from Spearman rank correlations were used to guide the choice of ancillary parameter to include in the CART model.[43] The dataset was complete in that all of the chemical concentrations were measured in each sample and even non-standard parameters were included, such as gene copies of *Dhc*.[43] It is very advantageous to have data regarding *Dhc* 16S rRNA, as *Dehalococcoides* is the only known microorgansism capable of complete dechlorination of PCE to ethene/ane. The difference between our data mining approach and the one used by Lee *et al*. is that our approach addresses what to do when the data is not as well behaved, which is the case for most environmental data. PMF essentially smooths the dataset so the data is more easily interpretable and capable of being worked with in the manner that we have presented. PMF is also useful in that it

apportions the data for you. Lee *et al*. assigned dechlorination potentials to use in the CART model[43], whereas PMF apportions the data into factors and takes classification out of your hands.

3.5 Conclusions

There is a thermodynamic hierarchy of electron accepting processes in the subsurface and the energetic favorability of dehalorespiration falls between iron-reduction and sulfate-reduction, with methanogenesis falling last on the spectrum.[61, 63] Groundwater systems are complex and dynamic in nature and multiple processes could be taking place at once in a given portion of an aquifer system. The remnants of chemical species can be products of multiple processes as a sample is merely a snapshot of a much larger motion in progress. The PMF model is a source apportionment tool and these processes can be considered as separate 'sources'. Thus PMF offers a unique ability to resolve otherwise intractable combinations of processes.

Analysis of the chlorinated ethene dataset provides indications of degradation via microbial dechlorination in the subsurface. The PMF method has been shown to be applicable and robust despite challenges such as missing data and inconsistent detection limits due to changing analysis methods. The PMF analysis of the chlorinated ethene data resolves a complicated data set into three factors representing parent contaminants (PCE and TCE) and two different extents of dechlorination. The fact that two dechlorination factors are identified suggests that there may be two pathways for dechlorination, or different microbial populations are responsible (sulfate reducers vs.

Dehalococcoides and *Dehalobacter*) or that one of the dechlorination factors represents a more advanced stage of dechlorination than the other. The model output is used to estimate how much of the mass of these compounds comes from dechlorination versus how much is attributable to other sources. The results suggest partial and advanced dechlorination may occur in different locations under different conditions. Results from correlation analysis performed on model output agree with the current understanding of microbial reductive dechlorination of chlorinated ethenes in the subsurface. Partial CE-dechlorination may occur under iron and sulfate-reducing conditions, whereas advanced dechlorination of vinyl chloride to ethene+ane require a more reducing environment as seen under methanogenic conditions.
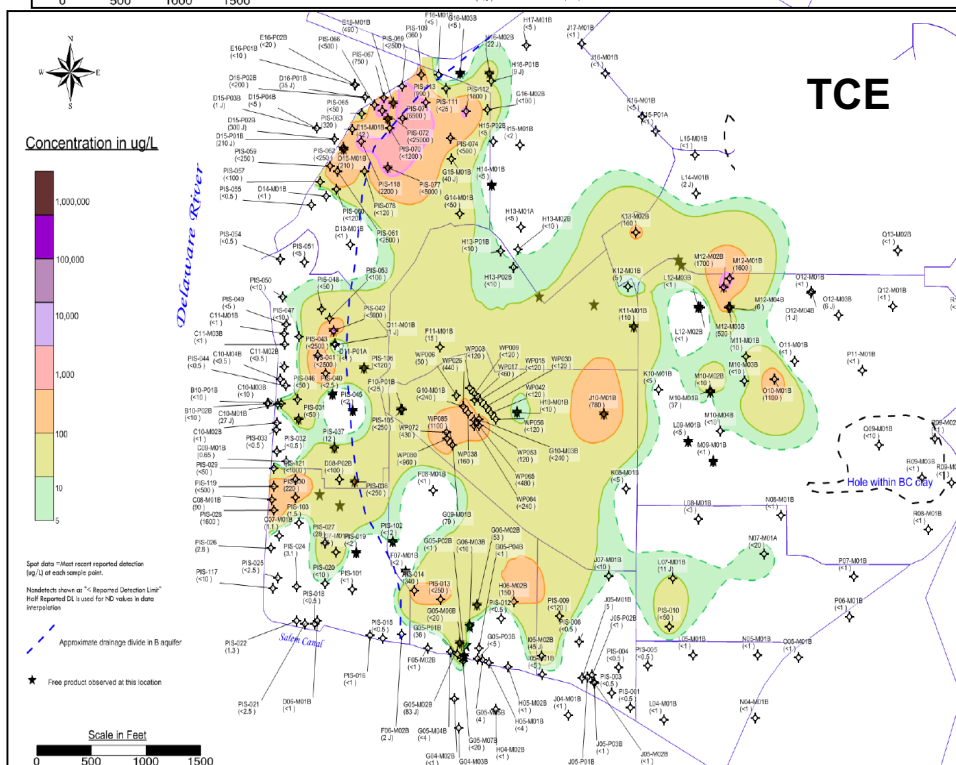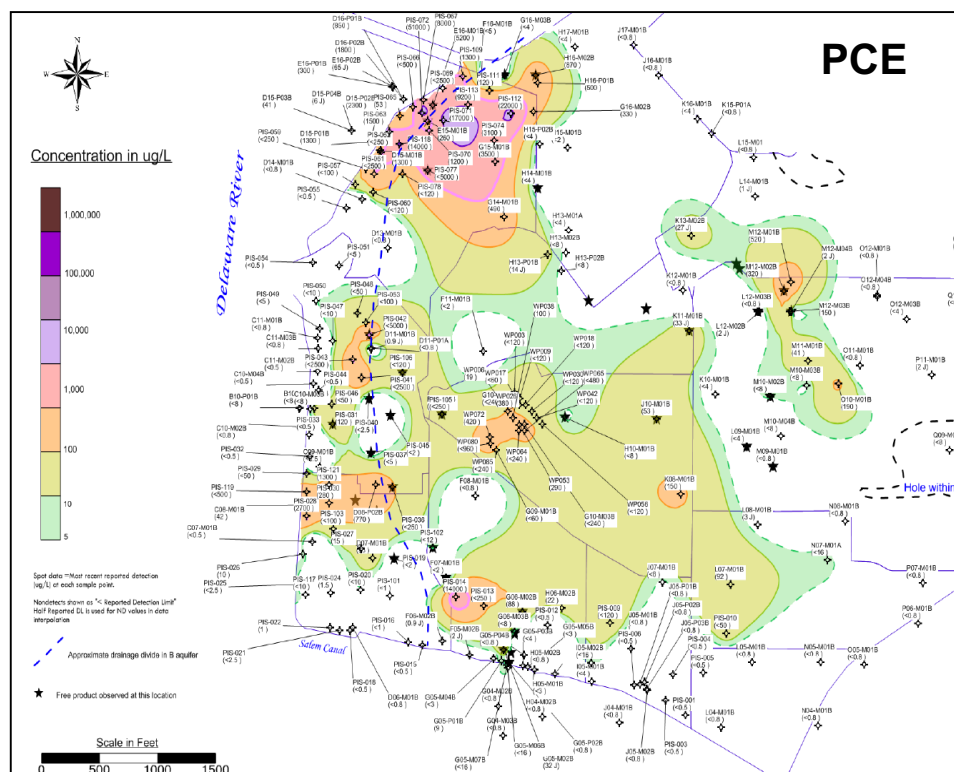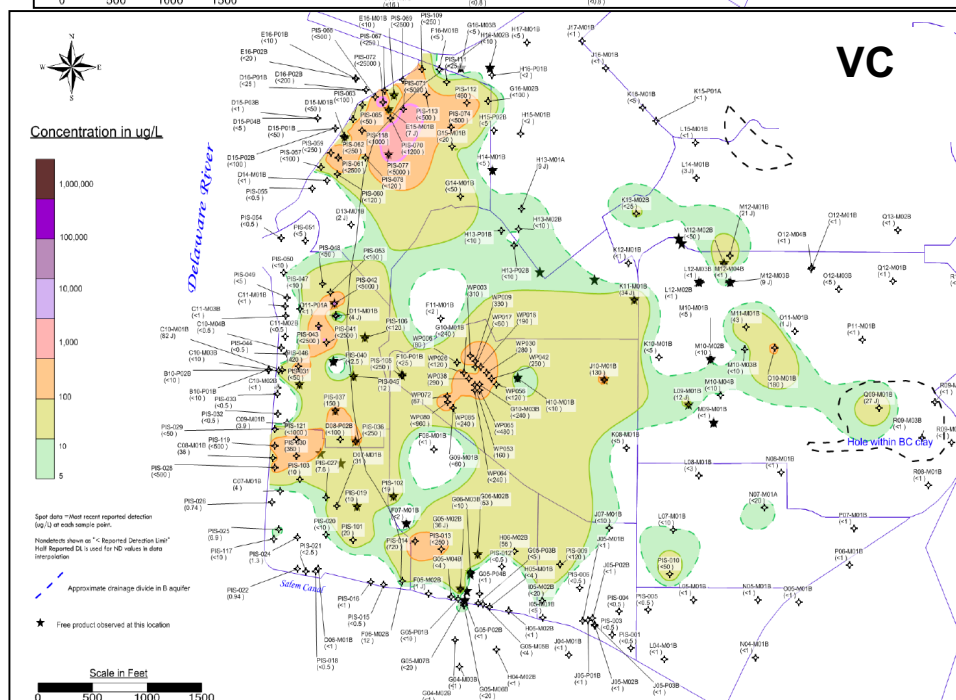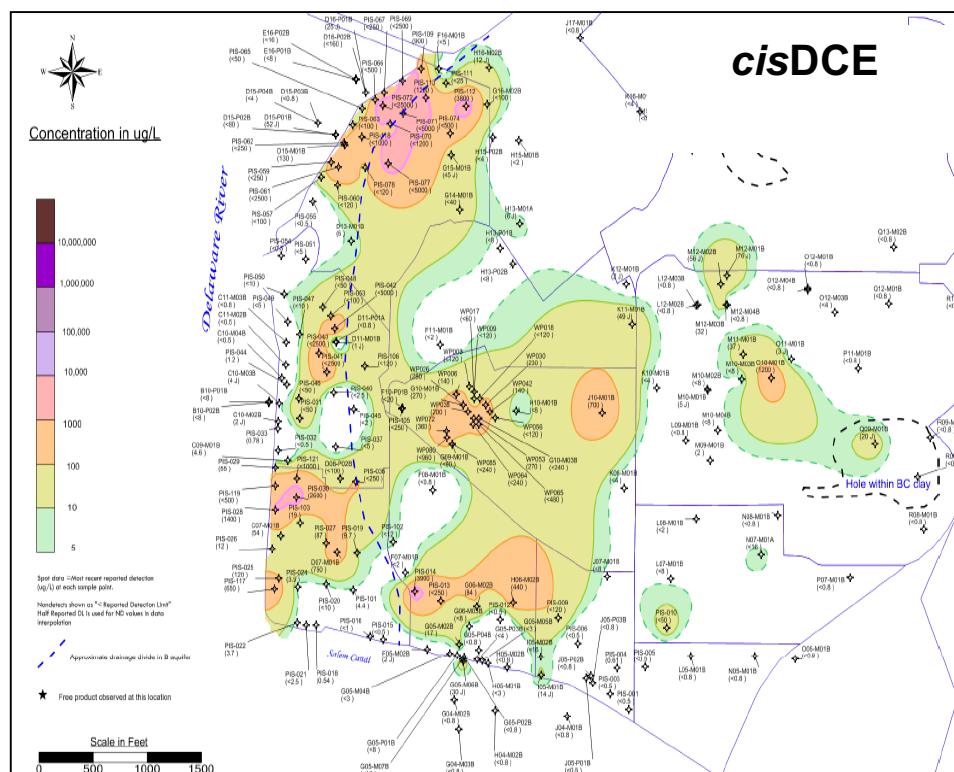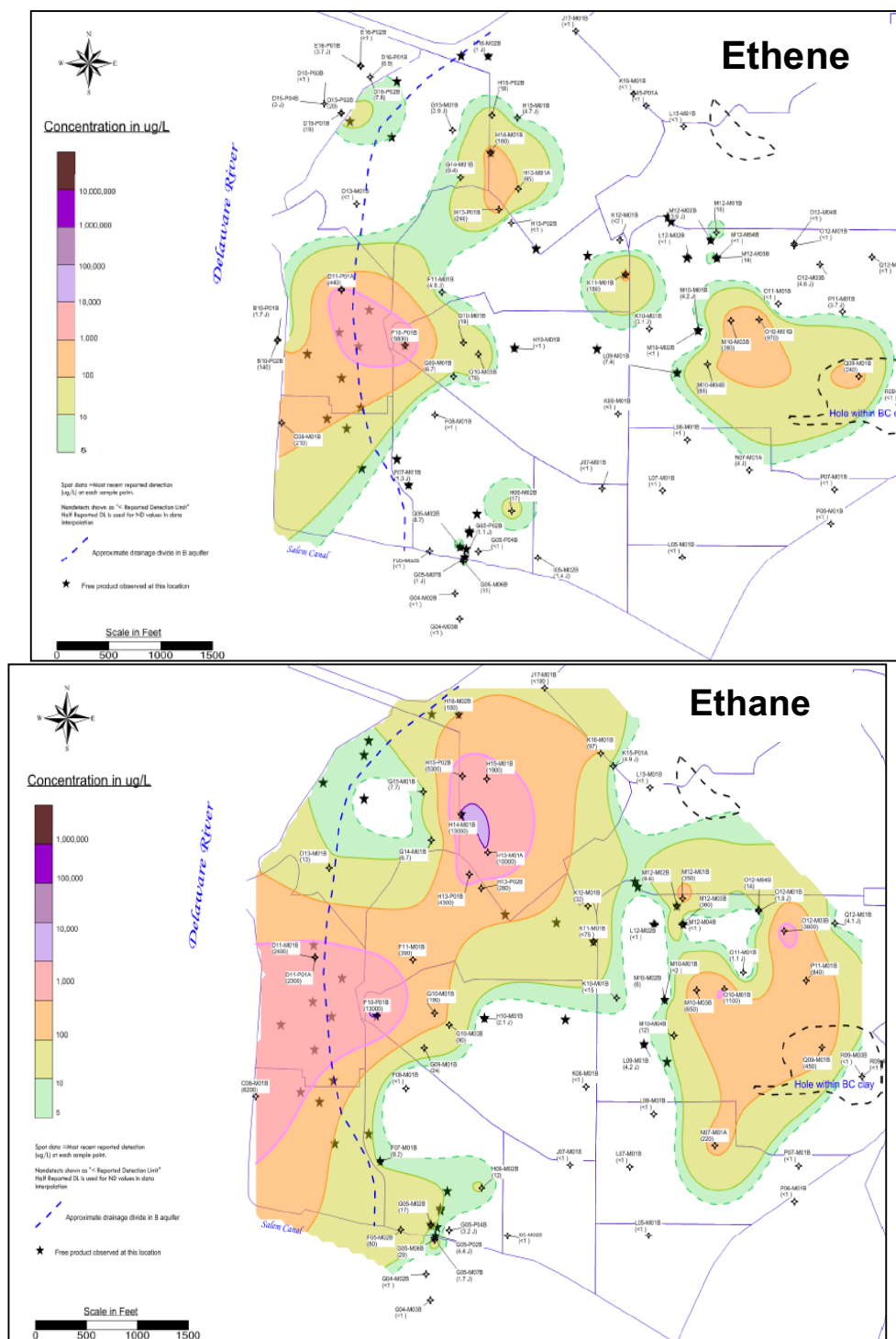
Figure 3-1. Groundwater plumes of the chlorinated ethenes, including ethene and ethane, located in the B-aquifer onsite. Maps prepared by URS on September 19, 2011 for an interior investigation report.[64]
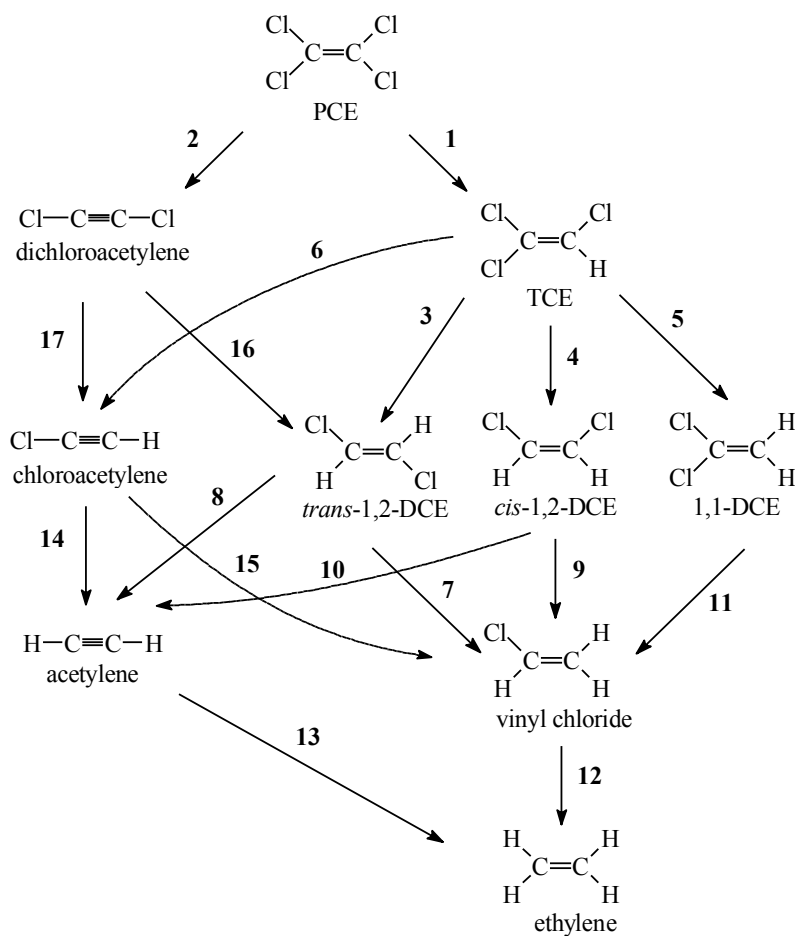
Figure 3-2. Abiotic and biotic anaerobic degradation pathways for chlorinated ethenes and related compounds.[65] Arrows 2, 17, 14, and 13 are abiotic pathways, whereas the rest are associated with biological transformations.
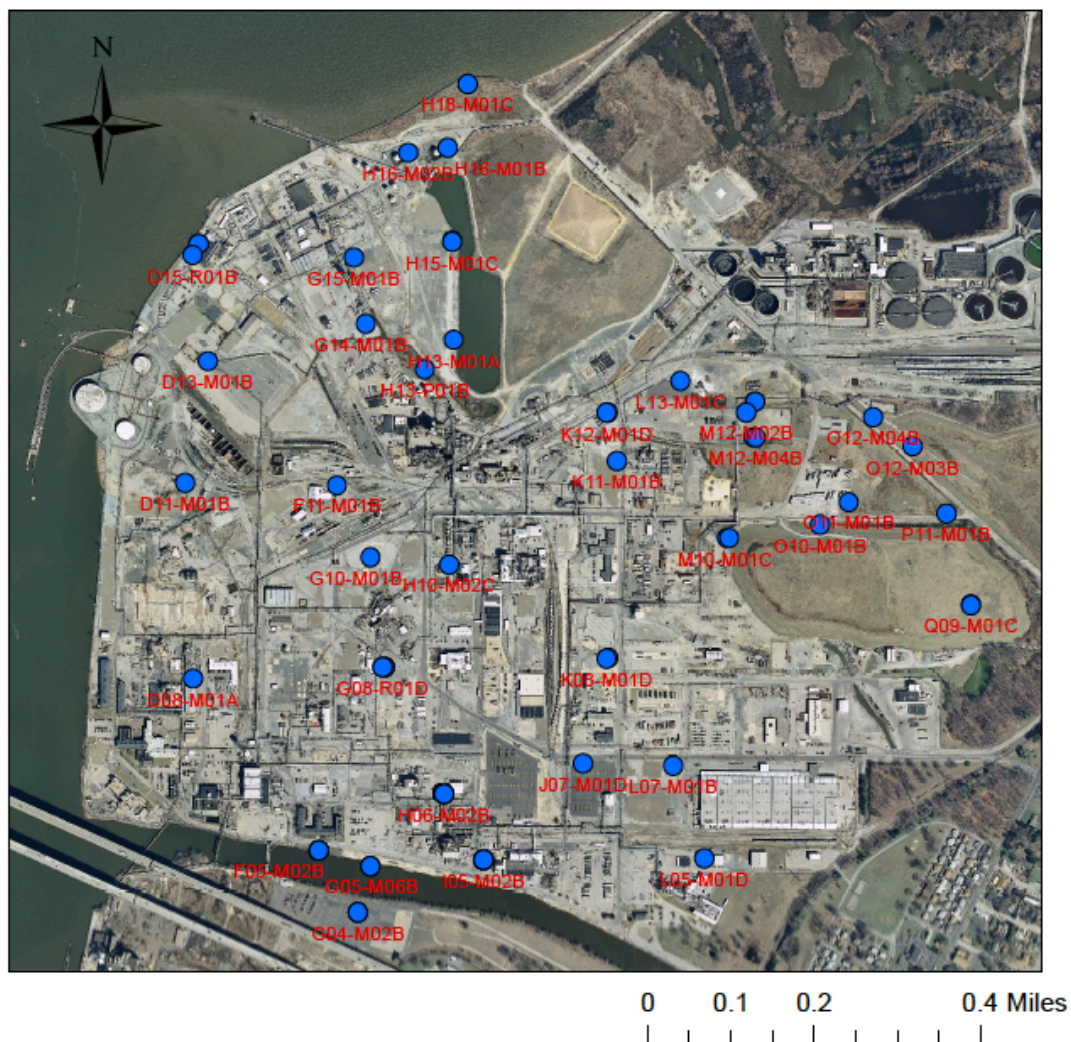
Figure 3-3. Satellite image of the site displaying the layout of the monitoring wells (blue dots) considered in the PMF2 investigation.
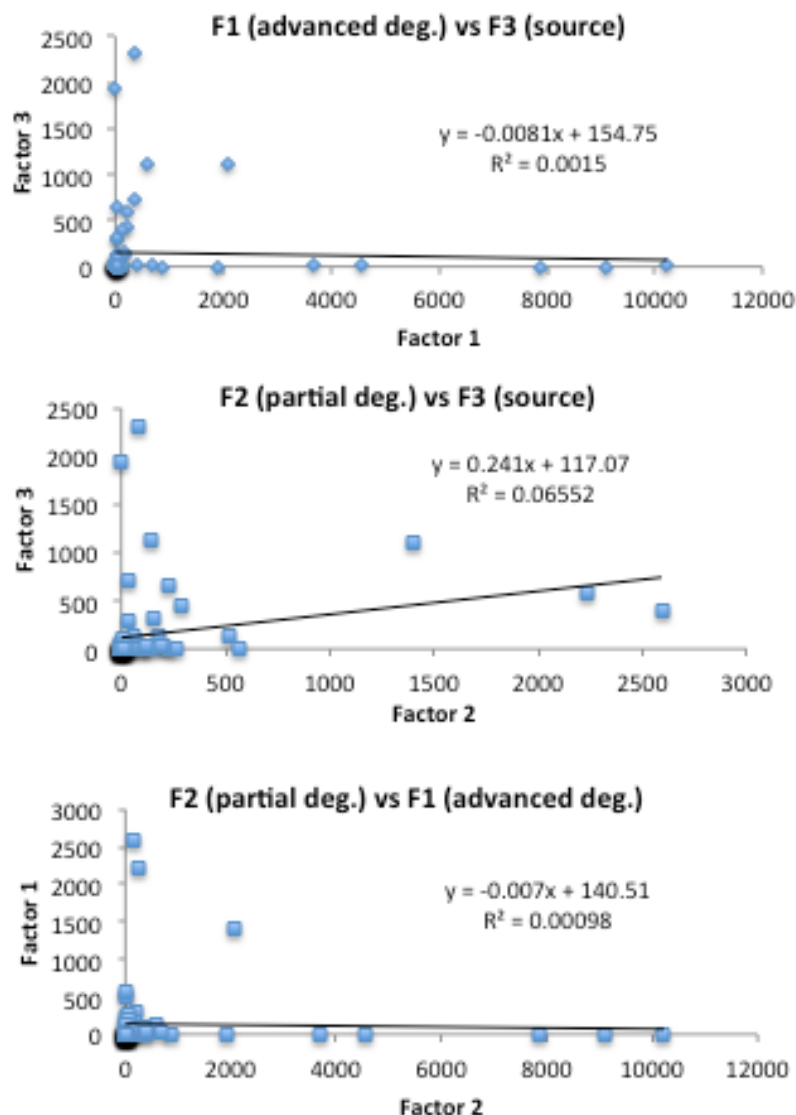
Figure 3-4. **G-space plots of each factor versus another for the 3-factor PMF solution. When factors are independent of each other, these plots should show wide scatter of data points, covering virtually all of the space between the axes, and there should be no correlation between the X and Y of each plot. The plots show a wide scatter of point with many points on and near the X-axis and Y-axis, indicating that the factors are independent of each other and rotation of the data matrix is not required.**
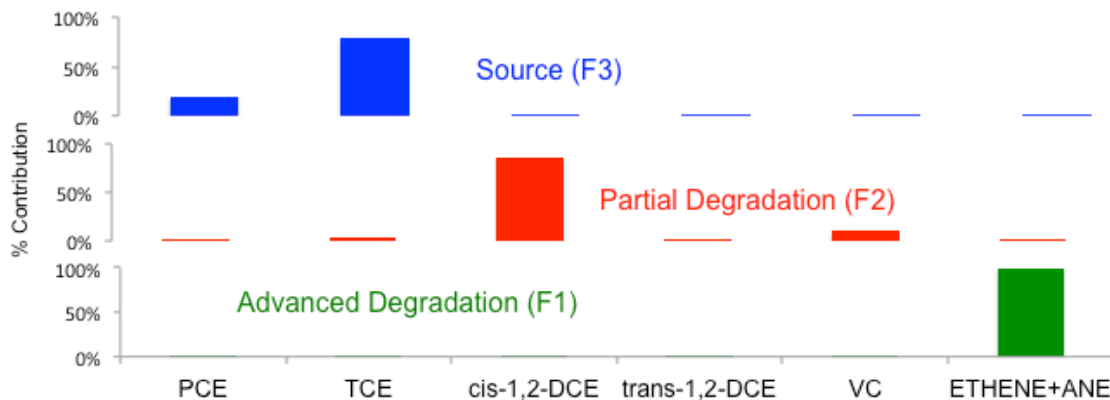
Figure 3-5. Chlorinated ethene source profiles of the 3-factors generated by PMF modeling.
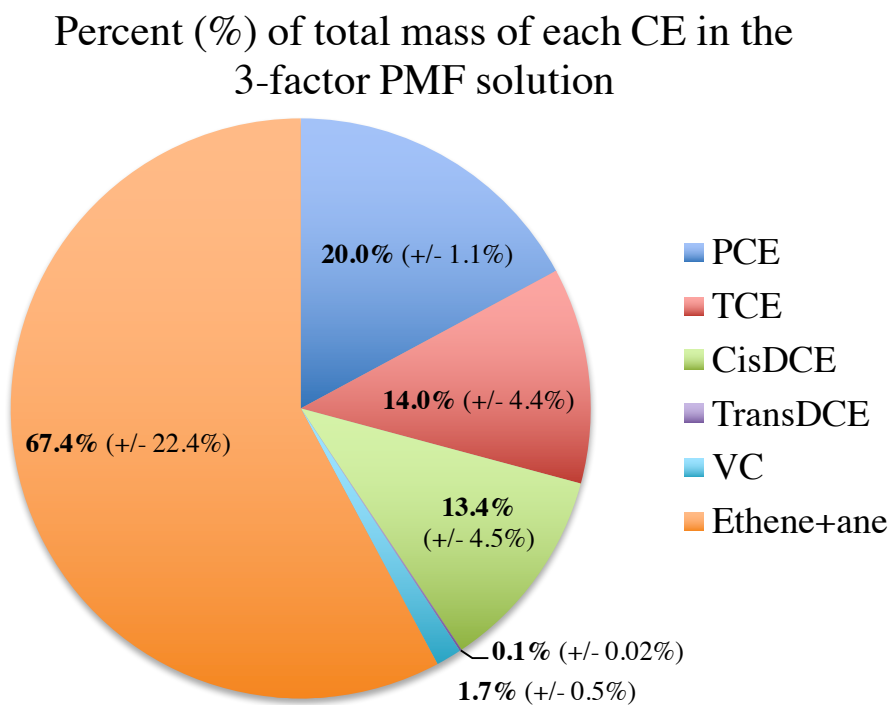
Figure 3-6. The percent (%) of total mass in the dataset that each analyte represents for the PMF2 model. The standard error is indicated in parenthesis.
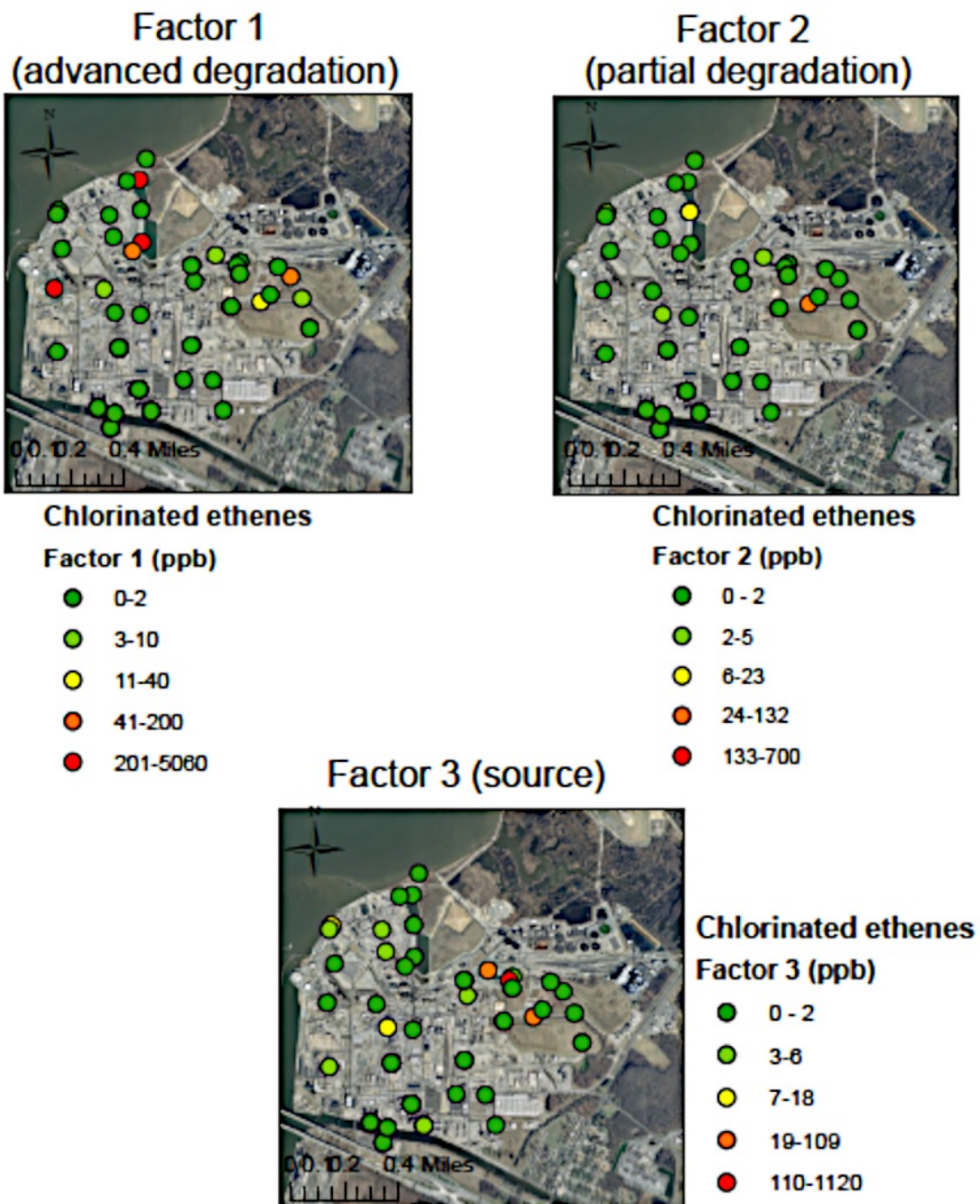
Figure 3-7. The absolute concentration (ug/L) of each factor profile in wells throughout all years considered. The scale for the legend was set up in percentiles (e.g., 20th, 40th, 60th, 80th, and 99th).
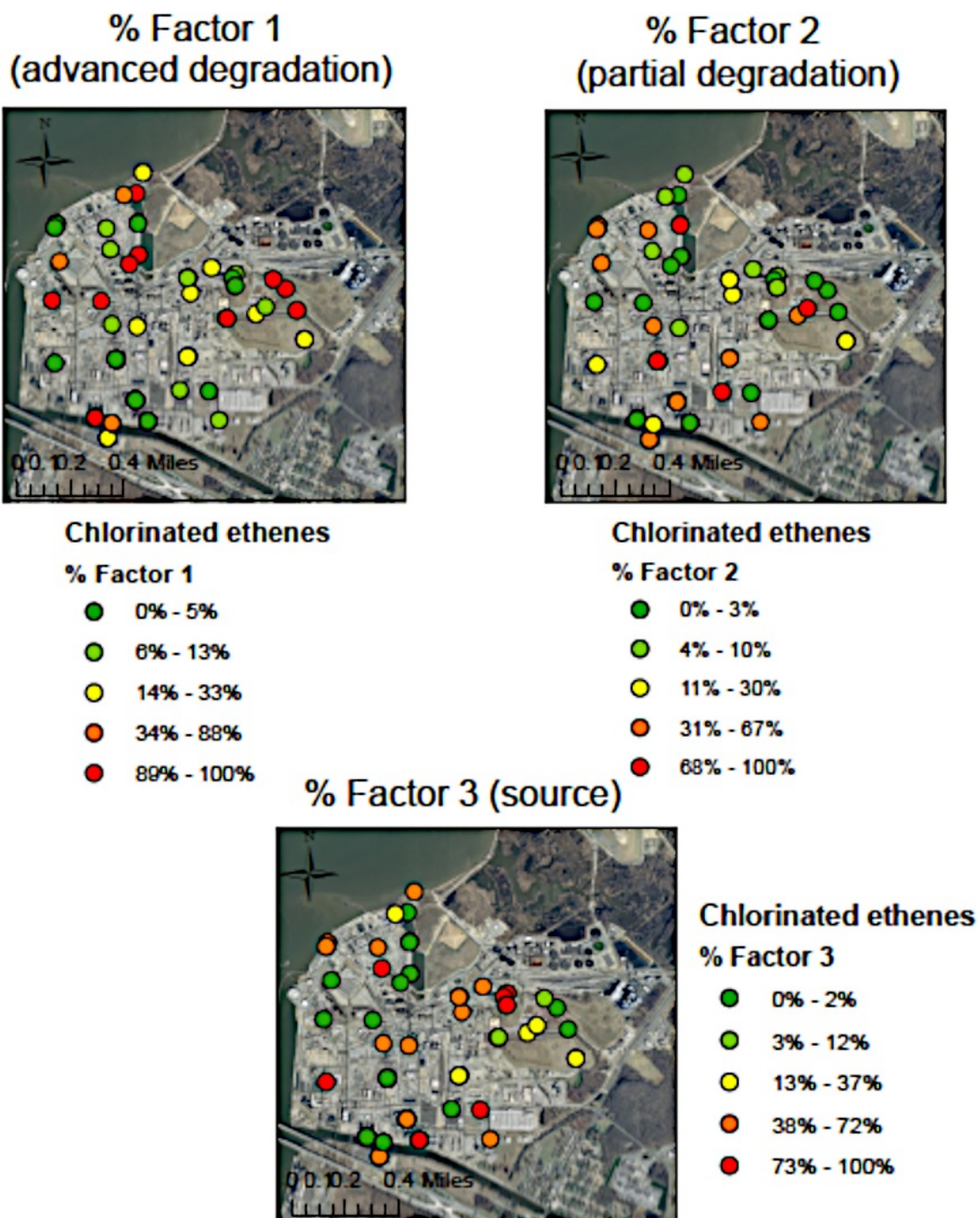
Figure 3-8. The percent of total contribution (%) of each factor profile in wells throughout all years considered. The scale for the legend was set up in percentiles (e.g., 20th, 40th, 60th, 80th, and 99th).
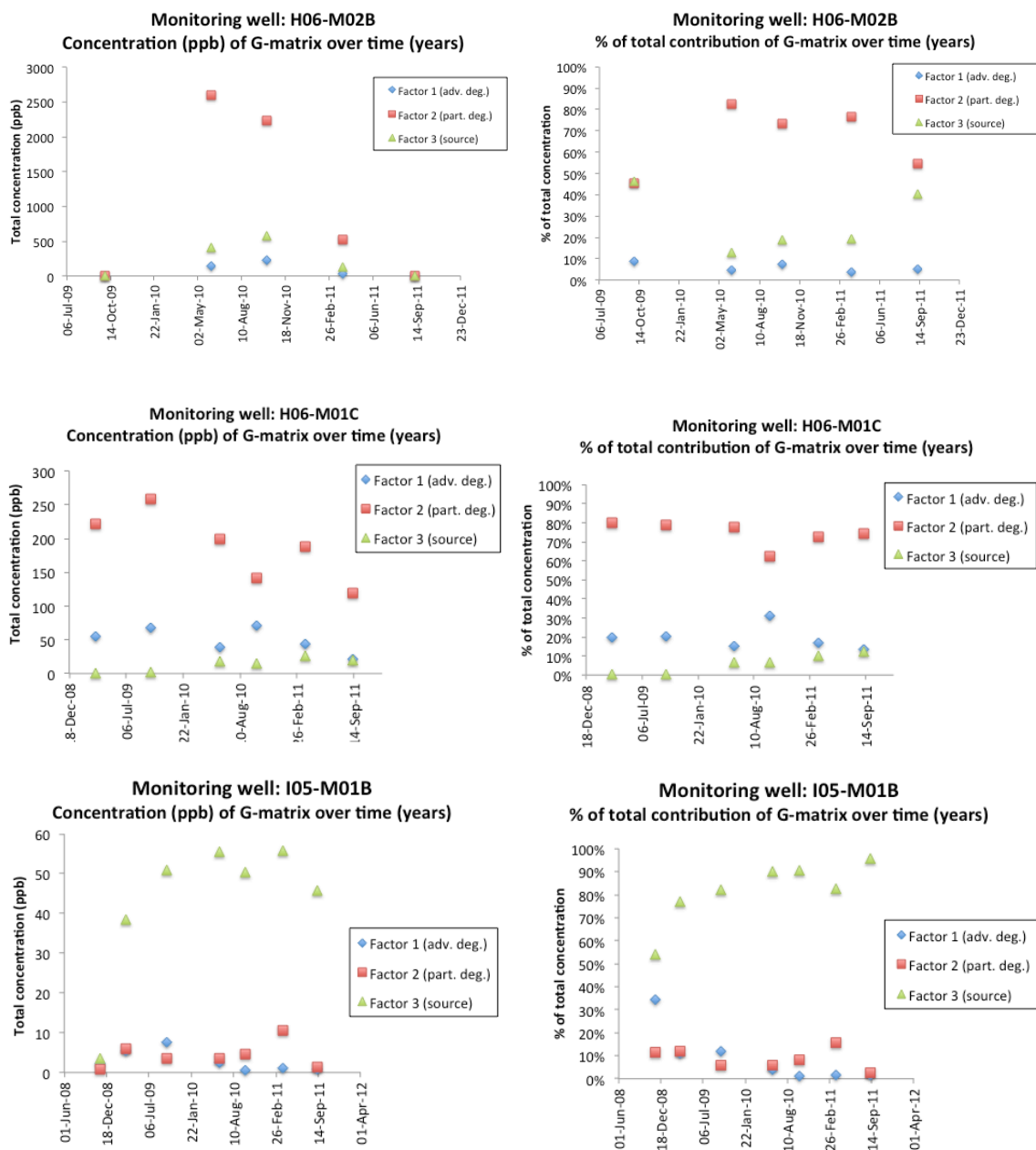
Figure 3-9. Temporal trends of the distribution of the G-matrix of each factor (absolute and normalized concentrations) in select monitoring wells with > 5 sampling dates.

Ferrous Iron

CEs_ferrous
Ferrous Fe

- 28 - 6200
- 6201 - 17700
- 17701 - 34700
- 34701 - 71900
- 71901 - 173000

Ferric Iron

CEs_ferric
Ferric Fe

- 260 - 19600
- 19601 - 54000
- 54001 - 119000
- 119001 - 256000
- 256001 - 943000
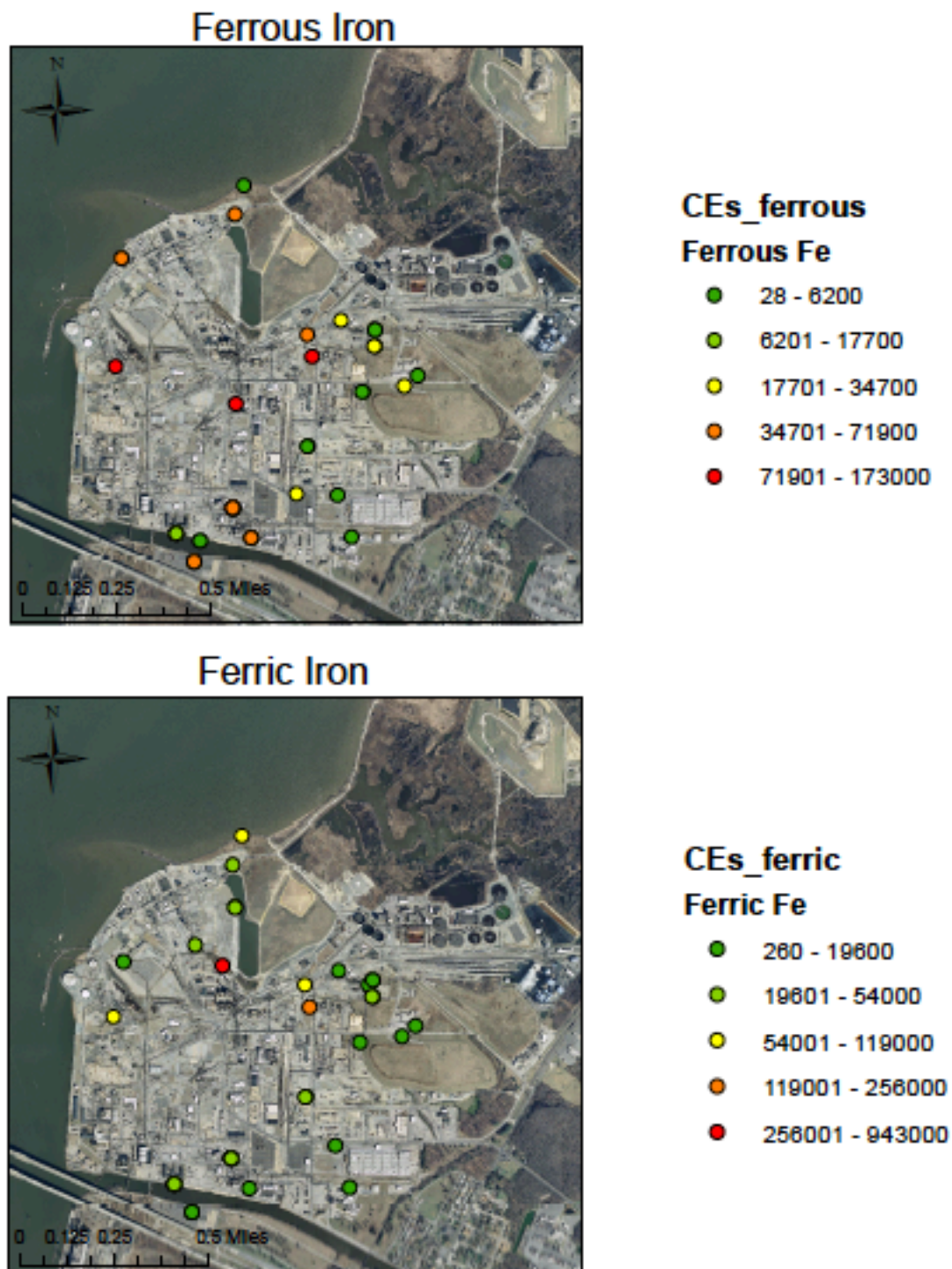
Figure 3-10. The concentration (ug/L) of ferrous and ferric iron in monitoring wells considered in the chlorinated ethene factor analysis solution.
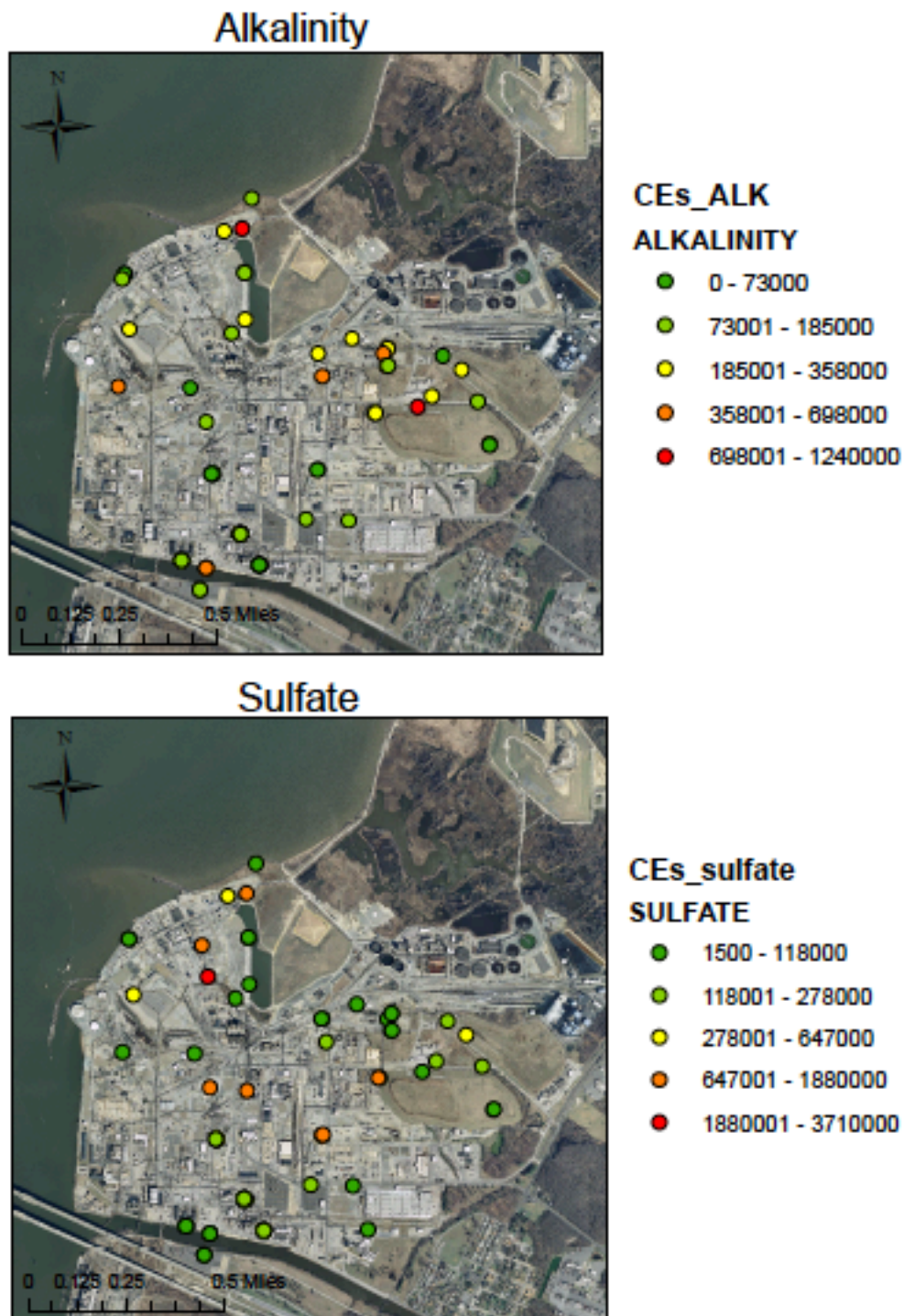
Figure 3-11. The concentration (ug/L) of total alkalinity and sulfate in monitoring wells considered in the chlorinated ethene factor analysis solution.
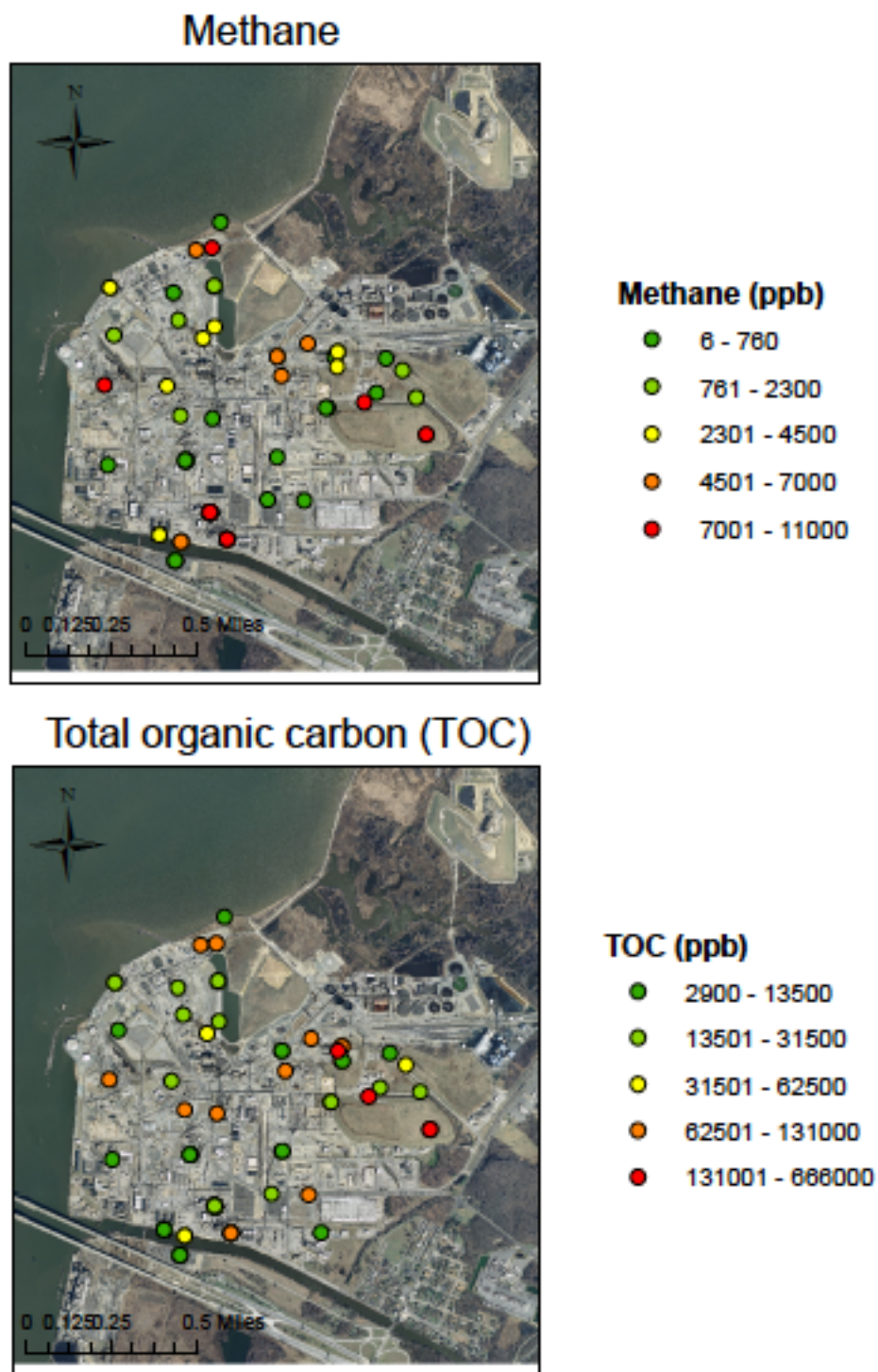
Figure 3-12. The concentration (ug/L) of methane and TOC in monitoring wells considered in the chlorinated ethene factor analysis solution.
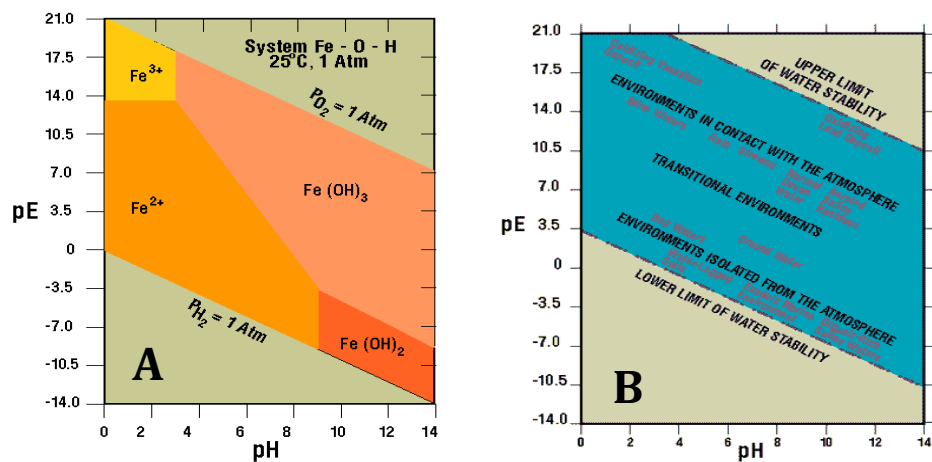
Figure 3-13. Stability-field diagram (A) for iron in the presence of water at 1 atm and 25ºC and (B) illustration of transitional oxidizing and reducing conditions in the environment.[66]

Table 3-1. Distribution of investigated CE and ancillary concentration data regarding each analyte included in the PMF model. The 10th, 50th, and 90th percentile concentrations (the Xth percentile concentration is that for which X% of the measured concentrations were lower) are reported for each analyte in the dataset after preprocessing.

	10th %ile	50th %ile	90th %ile	Minimum detected	Maximum	Mean
PCE (ug/L)	1.2	19	514	0.9	3,500	315
TCE (ug/L)	2.3	22.5	562	1	1,700	174
cisDCE (ug/L)	2	25	223	1	2,300	152
transDCE (ug/L)	1	4	13	0.9	21	6
VC (ug/L)	1	9	140	1	260	40
Ethene+ane (ug/L)	2	31	1,162	1.1	10,095	663
Alkalinity (ug/L as CaCO3)	40,700	116,000	405,600	10,200	1,240,000	204,277
TOC (ug/L)	5,320	18,600	96,160	2,900	666,000	62,377
Ferrous iron (ug/L)	523	23,150	59,800	28	173,00	30,150
Ferric iron (ug/L)	1,500	14,300	68,840	260	943,000	50,463
Methane (ug/L)	61	2,100	7,060	5.6	11,000	2,960
Nitrite (ug/L)	24	87	239	16	550	115
Sulfate (ug/L)	30,400	146,500	627,400	1,500	3,710,000	283,541
Sulfide (ug/L)	75.8	320	5,100	56	19,400	1,948
Temperature (ºC)	14	16	20	11	24	17
pH	4.93	6.23	7.22	3.59	8.33	6.17
redox potential (mV)	-127.86	-36.6	45.08	-274.5	187	-34.2
Aniline (ug/L)	7	93	8,540	0.7	63,000	3,881
Nitrobenzene (ug/L)	3.8	60	1,680	0.8	4,500	500

Table 3-2. The 6 analytes included in the PMF chlorinated ethene investigation and their chemical structure, molecular weight (MW) and the log of their octanol-water partition coefficients (log K_{ow}). MW and log K_{ow} values obtained from U.S. EPA KOWWIN software version 1.67.
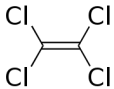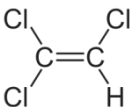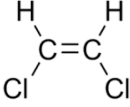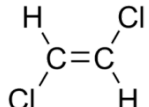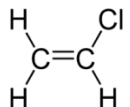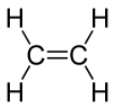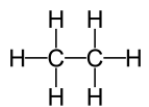
Chemical Name	MW (amu)	log K_{ow} (unitless)	K_H (atm*m^3/mole)	Chemical Structure
Tetrachloroethene (PCE)	165.83	2.97	1.77×10^{-2}	
Trichloroethene (TCE)	131.40	2.47	9.85×10^{-3}	
cis-1,2-Dichloroethene (*cis*DCE)	96.95	1.86	4.08×10^{-2}	
trans-1,2-Dichloroethene (*trans*DCE)	96.95	2.09	9.38×10^{-2}	
Vinyl Chloride (VC)	62.50	1.62	2.78×10^{-2}	
Ethene	28.05	1.26	2.28×10^{-1}	
Ethane	30.07	1.32	5.00×10^{-1}	

Table 3-3.   Applied uncertainty values for each investigated analyte in the PMF analysis. The base uncertainty, X, values was assigned to measurements of each detected analyte and an uncertainty value, 3X, was assigned to measurements below the limit of detection.

	PCE	TCE	*cis*DCE	*trans*DCE	VC	Ethene+ane
Base uncertainty, X	0.18	0.18	0.1	0.1	0.1	0.4
Uncertainty, 3X	0.54	0.54	0.3	0.3	0.3	1.2

Table 3-4. Spearman's Rank-Order Correlations for measured chlorinated ethenes: the rank of absolute concentration and percent of total mass of each analyte (after preprocessing of the data matrix) versus the rank of ancillary parameters. For those significant trends where p < 0.05, pink sign indicates a positive correlation, light blue indicates a negative correlation and no correlation are reported as yellow. For those significant trends where p < 0.005, red indicates a positive correlations and dark blue indicates a negative correlation and no correlation is reported as yellow. Note the units of ancillary parameters are ug/L except for T (C), pH, pE, and %AN, which are unitless.

Lower oxidation state of carbon ————→

More reducing ↓

parameter	n	PCE [C]	PCE %	TCE [C]	TCE %	cisDCE [C]	cisDCE %	transDCE [C]	transDCE %	VC [C]	VC %	Ethene+ane [C]	Ethene+ane %
pE	57	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	light blue
Nitrite	44	yellow	pink	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow
%AN	70	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow
Ferric Fe	38	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	pink
Ferrous Fe	44	yellow	light blue	yellow	yellow	red	yellow	yellow	light blue	red	yellow	red	yellow
Sulfate	75	yellow	dark blue	yellow	yellow	pink	pink	pink	yellow	yellow	yellow	yellow	yellow
Sulfide	35	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow
Methane	73	yellow	dark blue	red	yellow	pink	yellow	red	light blue	pink	yellow	red	yellow
Alkalinity	69	yellow	yellow	yellow	yellow	yellow	yellow	pink	light blue	pink	yellow	red	red
TOC	76	red	yellow	red	pink	pink	light blue	red	light blue	red	light blue	red	yellow
pH	57	light blue	yellow	light blue	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	red
Temperature	57	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow

Table 3-5. The relative standard deviation (RSD) of the G-matrix for model outputs requesting different numbers of factors, RSD of 10 model runs with random seed values.

Number of Factors	RSD of G Matrix (%)
2	0.7%
3	0.2%
4	61.6%
5	0.5%

Table 3-6. Correlation coefficients (r^2) for measured versus modeled concentration without outliers for the chlorinated ethenes. Outlier data points refer to those samples concentrations that are not adequately predicted by the PMF model and excluded from the regression. Note that plus signs (+) indicate high (> 50 ppb) concentrations and minus signs (-) indicate low (< 5 ug/L) or BDL concentrations for each outlier CE concentration.

Analytes	r^2 value	new r^2 value (excluding outliers)	Outlier concentrations (well name/sample date)
PCE	0.027	0.882	D08-M01A/ 11-04-2005 (+), D15-M01C/ 11-20-2008 (+), D15-M01C/ 02-09-2010 (+), D15-R01B/ 08-10-2011 (+), G14-M01B/ 06-14-2011 (+), G15-M01B/ 06-14-2011 (+), H15-M01B/ 06-14-2011 (-)
TCE	0.935	--	none
*cis*DCE	0.998	--	none
*trans*DCE	0.147	0.431	G05-M06B/ 09-09-2011 (-), H06-M02B/ 06-02-2010 (+), H06-M02B/ 10-06-2010 (+), M12-M01B/ 06-20-2011 (-), O10-M01B/ 06-22-2011 (-), Q09-M01C/ 04-23-2010 (-)
VC	0.676	0.875	G10-M03B/ 12-08-2010 (+), H06-M01C/ 03-19-2009 (+), H06-M02B/ 06-02-2010 (+), H15-M01C/ 06-14-2011 (-)
Ethene+ane	0.998	--	none

Table 3-7. Spearman's Rank-Order Correlations on model output: the rank of absolute concentration and percent of total mass of each factor versus the rank of ancillary parameters. For those significant trends where p < 0.05, pink sign indicates a positive correlation, light blue indicates a negative correlation and no correlation are reported as yellow.   For those significant trends where p < 0.005, red indicates a positive correlations and dark blue indicates a negative correlation and no correlation is reported as yellow. Note the units of ancillary parameters are ug/L except for T (C), pH, pE, and %AN, which are unitless.

Parameter	n	Source		Partial dechlorination		Advanced dechlorination	
		%	[C]	%	[C]	%	[C]
Redox, Eh	57	pink	yellow	yellow	yellow	light blue	yellow
Nitrite	44	yellow	yellow	yellow	yellow	yellow	yellow
%AN	70	yellow	yellow	yellow	yellow	yellow	yellow
Ferric Fe	38	yellow	yellow	yellow	yellow	pink	pink
Ferrous Fe	44	yellow	yellow	yellow	pink	yellow	red
Sulfate	75	yellow	yellow	red	red	dark blue	yellow
Sulfide	35	yellow	yellow	yellow	yellow	yellow	yellow
Methane	73	yellow	pink	yellow	yellow	yellow	red
Alkalinity	69	light blue	yellow	yellow	yellow	red	red
TOC	76	pink	red	dark blue	yellow	yellow	red
pH	57	light blue	light blue	yellow	yellow	red	yellow
Temperature	57	yellow	yellow	yellow	yellow	yellow	yellow

Table 3-8. Compilation chart of Spearman's Rank-Order Correlations for measured chlorinated ethenes and model output: the rank of *absolute* concentrations (ppb) versus ancillary parameters. Positive correlation, negative correlation, and no correlation are highlighted in green, red, and yellow respectively.

Analytes	PCE	TCE	*cis*DCE	*trans*DCE	VC	Ethene+ane
Ferric iron						
Ferrous iron						
Sulfate						
Methane						
Alkalinity						

PMF factors	Source	Partial dechlorination		Advanced dechlorination
Ferric iron				
Ferrous iron				
Sulfate				
Methane				
Alkalinity				

Table 3-9. Compilation chart of Spearman's Rank-Order Correlations for measured chlorinated ethenes and model output: the rank of *relative* concentrations (%) versus ancillary parameters. Positive correlation, negative correlation, and no correlation are highlighted in green, red, and yellow respectively.

Analytes	PCE	TCE	*cis*DCE	*trans*DCE	VC	Ethene+ane
Ferric iron	yellow	yellow	yellow	yellow	yellow	green
Ferrous iron	red	red	yellow	red	yellow	yellow
Sulfate	red	red	green	yellow	yellow	yellow
Methane	red	red	yellow	red	yellow	yellow
Alkalinity	yellow	yellow	yellow	red	yellow	green

PMF factors	Source	Partial dechlorination	Advanced dechlorination
Ferric iron	yellow	yellow	green
Ferrous iron	yellow	yellow	yellow
Sulfate	yellow	green	red
Methane	yellow	yellow	yellow
Alkalinity	red	yellow	green

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Chapter 4: Halomethanes

Abstract

Chlorinated methanes are common groundwater contaminants in the United States, and demonstrating whether they undergo degradation in the subsurface is important in determining the best remedy for this contamination. The purpose of this work was to use a new approach to investigate chlorinated methane degradation pathways in the subsurface. Positive Matrix Factorization (PMF) was applied to monitoring data regarding chlorinated methanes measured in groundwater at the Chambers Works facility in order to consolidate observations into a smaller number of more easily interpreted factors. A dataset containing concentrations of 5 halogenated methanes in 87 aqueous groundwater samples, collected from over 50 wells between 1990 and 2011, was investigated using PMF2 software. Despite the many shortcomings of this dataset, including missing analytes, quality assurance parameters, and method information, PMF analysis revealed a logical story of microbial dechlorination in the groundwater which provides insight as to where dechlorination is occurring, to what extent and under which conditions. PMF resolved two factors indicative of sources of carbon tetrachloride and chloroform and one factor representing dechlorination. Factors were further interpreted using ancillary data such as redox indicators and field parameters also measured in the samples. Due to the limited availability of supportive ancillary parameters for this dataset, results are not clear as to which redox conditions support dechlorination. PMF has still been shown to be a useful tool for investigating chlorinated methane dechlorination despite the heterogeneity of groundwater monitoring data.

4.1 Introduction

Chlorinated methane including carbon tetrachloride and chloroform are organic solvents commonly found in groundwater near historic industrial waste sites.[1, 2] Carbon tetrachloride is highly toxic to the liver and classified as a potential human carcinogen. [1, 2] Carbon tetrachloride and trichloromethane (chloroform) are used as industrial solvents and chemical intermediates in the production of refrigerants and carbon tetrachloride is also used as a commercial degreaser.[1] The compounds were historically used to manufacture refrigerants at the Chambers Works facility.

Chlorinated methane including carbon tetrachloride and chloroform, and breakdown product dichloromethane, are found in over 50 wells onsite (Figure 4-1) at levels exceeding the New Jersey Department of Environmental Protection (NJ DEP) groundwater standards, which are presented below in Section 4.3.1. Chlorinated methane concentrations have been measured in groundwater wells at Chambers Works for over two decades. Carbon tetrachloride is detected in the groundwater throughout the southwestern portion of the site (most notably in the Fluoroproducts area), where its presence is attributed to onsite use (Figure 4-2). The environmental distribution of chlorinated methanes at the subject facility is a basis for concern due to the possibility of chronic exposure and its effects on human health.

4.1.1 Properties and Reaction Pathways of Halomethanes

Halomethanes are volatile liquids and therefore can partition into air, causing issues with vapor intrusion in overlying structures. In addition, carbon tetrachloride and chloroform

are persistent in soil and slightly soluble in water, causing them to be especially

problematic in subsurface systems. The compounds are classified as a Dense Non-

Aqueous Phase Liquids (DNAPL) and tend to sink to the bottom of aquifers at or near the

point of entry, creating liquid pools of product that gradually dissolve into the

groundwater. In addition to sorption, halomethanes undergo various abiotic and biotic

transformations in the subsurface.[3] Carbon tetrachloride does not readily undergo

aerobic transformation [4], therefore anaerobic abiotic and biotic transformation

pathways are most relevant in the subsurface. Carbon tetrachloride undergoes abiotic and

microbial dechlorination in the subsurface resulting in a variety of transformation

products (Figure 4-3).[1, 2] Carbon tetrachloride can be transformed abiotically by

hydrolyzing to carbon dioxide, or it can be transformed under reducing conditions to

chloroform and carbon disulfide.[2] Microbially-mediated anaerobic transformation of

carbon tetrachloride include metabolic and co-metabolic reductive dechlorination

resulting in the systematic removal of the chlorine atom on the aliphatic compound as the

reaction proceeds.[5] Anaerobic reductive dechlorination of carbon tetrachloride and

chloroform have shown to occur in laboratory experiments under various reducing

regimes including, nitrate-reducing, iron-reducing, sulfate-reducing, methanogenic and

fermenting conditions.[1, 3, 6-12] The presence of carbon tetrachloride and chloroform

inhibit certain dehalorespiring bacteria such as *Dehalococcoides*, which are versatile

dechlorinators.

4.1.2 Goals of This Work

Thus the goals of this work are to: a) determine whether the Chambers Works data is of sufficient quality to be successfully analyzed by PMF; b) determine whether PMF can give useful information of microbial degradation processes in groundwater; c) investigate where and when microbial degradation of halomethanes occurred in the subsurface at Chambers Works; and d) investigate correlations between PMF outputs related to microbial degradation and ancillary parameters such as temperature, redox indicators and alkalinity in order to understand which conditions favor microbial degradation. We know dechlorination is occurring in the subsurface at the site which is why we are further examining dechlorination using this intimate data mining approach.

4.2 Methods

4.2.1 Analytes in PMF Analysis

A wide variety of chlorinated solvent groundwater contaminants have been measured at Chambers Works and these data are stored in the Envista database. In this study, we focus on the halomethanes. The measured compounds of interest include dibromochloromethane (DBCM), bromodichloromethane (BDCM), carbon tetrachloride (CT), chloroform (CF), and dichloromethane (DCM; Table 4-1). It should be noted that there was either too few measurements or too few detected measurements of bromoform (n = 2), chloromethane (n = 8), and methane (n=7) to include in the PMF analysis. Measurements of each compound taken as early as 1990 are present in the database. Various methods were used to measure the halomethanes in aqueous phase groundwater. The 1991 EPA method 8260 (Revision B) was used to measure the halomethanes with

the exception of a few samples collected in 1994, in which EPA Method 8240

(Revision A) was used. Details regarding EPA method 8240 and 8260 are provided in

Chapter 3. No data regarding internal standards or surrogates were available in the

database. In addition, ETC laboratories was used to analzye all groundwater samples for

halomethanes from 1990 until 1994. Lancaster laboratories analyzed samples collected

between 1994 and 2011.

4.2.2 Ancillary Parameters

Ancillary parameters were used to understand and correlate the PMF results, including

temperature (T, n = 41), pH (n = 41), redox (pE, n = 35), dissolved oxygen (DO, n = 41),

alkalinity (ALK, n = 14), total organic carbon (TOC, n = 48), sulfate (SO_4^{2+}, n = 21),

ferric iron (Fe^{3+}, n = 55), and the fraction of aniline and the sum of aniline and

nitrobenzene (%AN, n= 53), which is also used as a redox indicator here and previously

described in Chapter 1. Analytical methods by which these ancillary parameters were

measured in groundwater are also reported in Chapter 1. Unfortunately, for several

crucial ancillary parameters, not enough data was available to allow investigation of

correlations, including sulfate (n = 3), ferrous iron (n = 0), nitrate (n = 1), nitrite (n = 7),

methane (n = 7), and carbon dioxide (n = 7).

4.2.3 PMF Input Data Matrices

Groundwater data regarding halomethanes measured in aquifers A, B, C, D, and E

between 1990 and 2011 was extracted from the Envista database. A total of 87

groundwater water samples, in which 5 halomethanes were measured, were found in the

Envista database. More than 50% of the samples in the initial dataset were below the detection limit for DBCM, BDCM, CT and DCM. After removing samples in which more than half of the targeted halomethane analytes were not detected, as well as analytes that were BDL in most samples, the final dataset consisted of 5 analytes (Table 4-1) and 87 samples so that 42% of the measurements were BDL. This is higher than the chlorinated benzene (Chapter 2) and chlorinated ethene (Chapter 3) data sets in which 12% and 37% of measurements were BDL, respectively. As a result, aqueous phase groundwater concentration data ($X_{i,j}$) for 435 data points were submitted to PMF 2.0 software (YP-Tekniika KY Co., Helsinki, Finland). The collection dates of the samples range from June 1990 to August 2011.

For PMF2 analysis, three matrixes are submitted to the program: concentration, limits of detection (LOD), and uncertainty matrixes. The matrixes for the halogenated methanes were constructed in the same way as for the chlorinated ethenes and benzenes. Namely, for the concentration matrix, BDL values were replaced with a random number between zero and the method detection limit (MDL). There were no non-measured ('missing') values in the concentration matrix. The LOD matrix was assembled with the reported MDLs for each data point. For the uncertainty matrix, a (x, 3x) matrix was used,[13-20], where x is the uncertainty assigned to all detected measurements and three times this value (3x) is assigned to all those measurements BDL. The calculated relative standard deviation (RSD) of the surrogate recoveries is frequently used as x [19, 20] , however no laboratory or field surrogate recoveries were available. Therefore we assigned an uncertainty value to each compound using our best judgment after reviewing the available information regarding physical-chemical properties and sample collection and

measurement. BDCM and CDBM were assigned an uncertainty value of 0.3

(dimensionless) for all those detected measurements. CT was assigned an uncertainty of

0.1, whereas CF and DCM were assigned an uncertainty of 0.15, and 0.2, respectively, to

all detected measurements. Again, all measurements BDL were assigned three times the

aforementioned uncertainty for each analyte. There is not a large range between these

uncertainty assignments of each investigated halomethane. We decided to assign a

higher uncertainty to BDCM and CDBM to these compounds' reactivity in the

subsurface. Brominated compounds are more easily dehalogenated because bromine is a

better leaving group in reductive dechlorination.[21]   In addition, BDCM and CDBM are

detected at much lower concentrations in comparison to the CT, CF and DCM (Table 4-

1). CT was assigned the lowest uncertainty because it is the least volatile.

4.2.4 Spatial Trends

The ArcGIS software (version 10.2.2) enabled us to map model solutions in over 50 wells

throughout 1990 and 2011 (Figure 4-1).

4.2.5 Correlation Analysis

Spearman's correlation of the strength of each factor in each sample (i.e., G-matrix or

mass contribution) was used to examine correlations with measurements of geochemical

and field data to examine locations where microbial dechlorination is occurring in the

subsurface. Further details of Spearman's correlations are provided in Chapter 3.

4.3 Results

4.3.1 Description of Datasets

The 10th, 50th, and 90th percentile concentrations (the Xth percentile concentration is that for which X% of the measured concentrations were lower) of the halogenated methanes as well as the ancillary parameters are reported in Table 4-2. The concentrations presented are after the data had been preprocessed for PMF analysis (i.e. BDL data replaced by a random number between zero and the MDL). Concentrations of carbon tetrachloride are highest in the northwest portion of the site (Figure 4-2). NJ Class IIA groundwater quality criteria for BDCM, CDBM, CT, CF and DCM are 0.6 µg/L, 0.4 µg/L, 0.4 µg/L, 70 µg/L, and 3 µg/L, respectively. Concentrations of BDCM range from 0.8 to 82 µg/L and CDBM concentrations range from 0.8 to 77 µg/L. Concentrations of CT, CF, and DCM range from 0.8 to 26,000 µg/L, 1 to 24,000 µg/L and 0.8 to 9,600 µg/L, respectively.

4.3.2 Correlations with Absolute Analyte Concentration Data

Spearman correlations were performed on the ranked absolute measured concentration (µg/L) data after preprocessing for PMF analysis as well as on *normalized* concentration data (Table 4-3). The results were compared with similar correlations between ancillary measurements and the PMF results to determine whether PMF analysis contributed to a better understanding of the data than careful examination alone.

The following bulleted list compares the results from correlation analysis of ancillary measurements including geochemical data and redox indicators versus absolute

concentrations of the investigated analytes and the percent of total mass of each analyte (*relative* concentrations).

4.3.2.1 Geochemical Data & Redox Indicators

- Redox, Eh (field):   Redox showed no relationships with absolute or *relative* concentrations of the investigated analytes.

- %AN: %AN showed no relationships with absolute or *relative* concentrations of the investigated analytes.

- Nitrate: Nitrate showed no relationships with absolute or *relative* concentrations of the investigated analytes.

- Ferric iron: Correlations using absolute concentration of analytes show ferric iron is positively correlated with BDCM and negatively correlated with CT. The results using *relative* concentrations of analytes also show a negative relationship with CT. Dechlorination of CT can take place under iron-reducing conditions.[3, 8, 22]

- Sulfide: Results of correlations between sulfide and absolute concentrations of the analytes show a positive correlation between sulfide and CF. Correlations results with *relative* concentrations of the analytes and sulfide showed no relationships. Dechlorination of CF can occur under sulfate-reducing conditions.[3, 9]

4.3.2.2 Nutrients & Field Parameters

- Dissolved oxygen (DO): For absolute concentrations, DO was negatively

  correlated with CT. For relative concentrations, DO was positively correlated

  with BDCM and CDBM, but negatively correlated with CT. Dechlorination of

  CT occurs under reducing conditions.[3] Debromination and/or dechlorination of

  BDCM and CDBM may occur under lesser reducing (slightly oxidizing)

  conditions.[21]

- Alkalinity: Alkalinity showed no relationships with absolute or *relative*

  concentrations of the investigated analytes.

- Total organic carbon (TOC): For absolute concentrations, TOC showed no

  relationships with absolute or *relative* concentrations of the investigated analytes.

  For *relative* concentrations, TOC is negatively correlated with CT and positively

  correlated with DCM.

- pH: pH showed no relationships with absolute concentrations of the investigated

  analytes. For *relative* concentrations, pH is negatively correlated with DCM.

- Temperature: For absolute concentrations, temperature is positively correlated

  with CT and negatively correlated with DCM. For relative concentrations,

  temperature is positively correlated with BDCM, CDBM, CT, and negatively

  correlated with DCM. Microbial activity generally increases with increasing

  temperature[23], which could explain the positive correlation between

  temperature and parent compounds (such as CT) and the negative correlation with

  the dechlorination product (DCM). An alternate explanation for the negative

  relationship between DCM and temperature is volatilization. At higher

temperatures, DCM, will more readily volatilize out of aqueous solution during sample collection. In addition, the aqueous solubility of halomethanes increases with increasing temperature (assuming no increases in salinity).[21]

4.3.3 PMF Analysis

The PMF model was run requesting 2 to 5 factors starting at 10 different initialization points (seed values) for each requested number of factors. The 3-factor solution was determined to be the 'correct' number of factors for this dataset for the following six reasons outlined below. Three factors were resolved from the data set. Criteria used to determine the correct number of factors is detailed in Chapter 1. Results demonstrate that the quality of the data is sufficient that PMF analysis can be performed and can yield stable model solutions, which addresses the first objective, goal A, mentioned above.

- First, a MLR of the G matrix versus the sum of the measured concentrations of the analytes for the 3-factor solution showed all factors with positive and significant ($p < 0.05$) coefficients.

- Second, the model results are stable and reproducible. The average RSD of the G and F matrixes for all 10 seed runs in the 3-factor model are 1.8 % and 2.2 %, respectively (Table 4-4).

- Third, the resolved factors are independent. G-space plots were examined and indicate each factor is independent of each other and rotation of the data matrix is not necessary (Figure 4-4).

- Fourth, plots of modeled versus measured concentrations are in good agreement. The 3-factor model yielded an R^2 value better than 0.99 for all of the chloromethanes. The agreement was worse for the brominated compounds, but

after the exclusion of several outliers, the R^2 for CDBM was 0.67 (5 outliers) and

for BDCM was 0.60 (28 outliers). The agreement between measured and

modeled concentrations of the chloromethanes did not improve significantly when

4 factors were requested. In addition, the 4-factor model split the each of the

halomethanes into its own individual factor, which does not aid interpretation of

the results. Specifically, BDCM, CT, CF, and DCM are split into separate factors

in the 4-factor model solution.

- The fifth criterion for determining the correct number of factors is that results Q-

  plots indicate the PMF model converged on the 3-factor solution (Figure 4-5).

  The calculated Q value varies with the number of factors. In theory, the

  calculated Q should be equal to the theoretical Q when the correct number of

  factors has been chosen.[24] However, in many cases, especially when the

  uncertainty cannot be correctly estimated, the calculated Q value may deviate

  substantially from the theoretical one. When uncertainties are correctly estimated,

  Q-values can assist in guiding the judgment of the correct number of factors. [24]

- The sixth and final criterion for determining the correct number of factors is that

  the model results are physically meaningful and judged to be the most

  informative. Too many factors should not be requested for this data matrix

  because the dataset is small and contains only 5 analytes.

4.3.4 Halomethane Source Profiles

The PMF model resolved three source profiles (factors) in the groundwater monitoring

dataset of the halomethanes (Figure 4-6). Factor 1 is comprised of ~1:3 ratio of CT (CT)

and trichloromethane (CF) and constitutes 31% of the total mass of the solution (Figure

4-7 and Figure 4-8). Factor 1 also contains nearly all of the CT and 13% of CF in the data set. We conclude factor 1 may represent a source of halomethanes.

Factor 2 is comprised of ~100% CF and contains nearly all of BDCM and CDBM and ~74% of the CF in the data set. Factor 2 constitutes 43% of the total mass of the solution. Factor 2 may also represent a source of halomethanes in the groundwater onsite.

Factor 3 consists of ~1:3 ratio of CF and DCM contains virtually all of the DCM and 13% of the CF in the dataset. Factor 3 consists of 26% of the total mass of the solution. Factor 3 is believed to represent dechlorination of CT to form CF which is then reduced to DCM.

It is helpful to consider the octanol-water partition coefficient (K_{ow}) and the Henry's law constant (K_H) of each analyte (Table 4-1) in order to determine whether the factors are indicative of physical processes. K_{ow} is an indicator of the hydrophobicity of a chemical compound and K_H is an indicator of the volatility of a compound from aqueous solution.[25] The K_H values provides insight to how readily a chemical compound would volatilize out of the aqueous phase and into air. The K_{ow} values reveal how readily the compound would partition out of aqueous and onto organic material such as aquifer solids, biomass, or even DNAPL. If the concentrations of the analytes were primarily controlled by physico-chemical properties and the chromatography effect, CT would not be found in the same factor as CDBM or BDCM due to their different K_{ow} and K_H values. Futhermore, CT would not be found in the same factor as CF due to their different K_{ow}

and K_H values. The PMF results suggest the halomethane fingerprints are a product of microbial degradation processes rather than of their physical-chemical properties. Another important issue to discuss is the lack of mixing in the subsurface due to laminar flow of the groundwater, which is not an important issue here as the site has numerous pumping wells installed around the perimeter, that increase dispersion and thus mixing across the site. PMF results are interpretable and tell a relatively coherent story about the fate of halomethanes in the subsurface. PMF has not only proven to be a useful tool for analyzing groundwater data for chlorinated ethenes and chlorinated benzenes, but also useful for analyzing halomethanes. The above results address the second objective, goal B, of the work.

4.3.5 Temporal and Spatial Trends in PMF Factors

A total of 52 wells had enough data to assess spatial trends of the site-wide chlorinated benzene PMF solution (Figure 4-1). In Figure 4-9, the absolute concentration of each factor is displayed throughout the investigated years of the study between June 1990 and August 2011. The percent of the total of each factor in each well is displayed throughout the study period in Figure 4-10. Many 'hot spots' of the dechlorination factor (factor 3) occur along the perimeter of the site with a group occurring in the western corner adjacent to the Delaware River. Factor 1 (source of CT & CF) is most abundant in the northwestern and southwestern corners of the site, whereas the only 'hot spots' of factor 2 (source of CF), are spread out across the site with a large group in the southeastern portion of the site. Dechlorination may not be occurring in the southeast corner due to

improper physical condition or abiotic or biotic inhibition.

All three factors occur in similar places from each other except for the large grouping of wells high in CF. This makes sense since CF in known to inhibit reductive dechlorination by certain dechlorinators such as *Dehalococcoides*. [26] The following bulleted list consists of select wells, with at least 5 sampling events, in which temporal trends of the factors have been examined over time intervals considered in the study. The trends suggest dechlorination conditions differ not only by well location but also by time within locations, which addresses goal C of the work.

- Monitoring well G16-M03B is a B-aquifer well located in the western portion of the site adjacent to the Delaware River. The samples included in the study (n = 5) for G16-M03B were collected between July 1999 and July 2003 (Figure 4-11). Dechlorination (factor 3) of halomethanes appears to be occurring in G16-M03B and it is accompanied by the CF source (factor 2). Alkalinity, methane, ferrous iron and sulfide data are either below detection limit or not measured with the investigated analytes in the preprocessed PMF dataset for this well. Temperature data is available and values are as follows: 16.1C in July 1999 and 2000, 16.4C in July 2001, 19.3C in July 2002, 17.2C in July 2003. In addition the pH in G16-M03B is as follows: 5.03 in February 1996, 5.51 in July 1999, 5.37 in July 2000, 5.23 in July 2001, 5.52 in July 2002, and 5.35 in July 2003. Lastly, ferric iron concentrations were taken in well G16-M03B and reported as: 1,700 µg/L in April 1994, 2,800 µg/L in February 1996, 2,450 µg/L in November 2000, 2,080 µg/L in July 1999, 2,500 µg/L in July 2000, 2,400 µg/L in July 2001, 3,990 µg/L

in July 2002, and 2,750 µg/L in July 2003. %AN values are available and taken

during July and values are as follows: 0.23% in 1999, 0.30% in 2000, 0.05% in

2001, 0.09% in 2002, and 0.12% in 2003. There is not enough supplementary

data available to deduce the redox environment throughout the observation

period, although the %AN values suggest it is oxidizing. This is surprising given

that factor 3 (dechlorination) is prevalent in this well.

- Monitoring well D15-M01B is a B-aquifer well located in the western portion of

  the site adjacent to the Delaware River. The samples included in the study (n = 7)

  for D15-M01B were collected between July 1999 and July 2011 (Figure 4-12).

  Dechlorination of halomethanes (factor 3) appears to be occurring in D15-M01B

  and it is accompanied by both source terms, factor 1 (CT & CF) and factor 2 (CF).

  Alkalinity, methane, ferrous iron and sulfide aqueous concentration data are either

  below detection limit or not measured with the investigated analytes in the

  preprocessed PMF dataset for this well. pH was also measured during the

  following observation periods: 5.93 in July 1999, 6.06 in July 2000, 6.5.98 in

  July 2001, 6.09 in July 2002, 6.32 in July 2005, 5.59 in July 2007, and 5.68 in

  July 2011. The following ferric iron measurement were taken in the month of July

  and was 2,410 µg/L in 1999, 1,800 µg/L in 2000, 1,840 µg/L in 2001, 1,910 µg/L

  in 2002, 1,250 µg/L in 2005, 1,030 µg/L in 2007 and 240 µg/L in 2011.

  Temperature was 20.3 in July 2009, 19.3 in July 2000, 20.6 in July 2001, 23 in

  July 2002, 22.1 in July 2005, 20.7 in July 2007, and 20.0 in July 2011. %AN

  values are available and were taken in July and values are as follows: 60.4% in

1999, 77.8% in 2000, 92.3% in 2001, 83.8% in 2002, 100% in 2005, 98.4% in 2007 and 2011. Redox measurements indicate a shift in the redox environment between 2001 and 2007. Specifically redox measurements are as follows: 28 mV in 2001, -98.4 mV in 2002, 5 mV in 2005, and -103.2 mV in 2007. There is not enough supplementary data available to deduce the redox environment throughout the observation period but the % AN values suggest the well is probably reducing. The shift in redox and the ever increasing %AN ratio indicate that conditions in this well may have become more reducing over time. This is in agreement with the PMF results, which show an increasing contribution from factor 3 starting around 2001.

4.3.6 Spatial Trends of Ancillary Measurements

Spatial distribution of absolute concentration of various ancillary measurements was examined using ArcGIS software. The average concentrations of available geochemical, nutrient, and field data are plotted throughout the wells considered in the study and observations are presented below.

- pH: There is a large range of pH values in the data set (Figure 4-13). Areas that are more acidic (pH < 5.7) are grouped occurring in the western perimeter adjacent to the Delaware River, whereas areas that are less acidic (pH > 6.3) are located in the south and southern portions of the site.

- Temperature: The groundwater temperature generally appears to be higher further away from the center and warmer spots appear to make a circular pattern around the site (Figure 4-13).

- Total Organic Carbon (TOC): High concentrations of TOC (> 43,000 μ g/L)

  occur in the western corner of the site as well as the center in areas that are also

  high in factor 3 (dechlorination) (Figure 4-14).

- Ferric iron: Ferric iron concentration are highest (> 3,051 μ g/L) around the

  perimeter of the site.

4.3.7 Correlation Analysis

Spearman's rank-order correlations were performed in attempt to identify ancillary

parameters that are correlated with the various PMF factors, especially factors 3 which is

indicative of dechlorination. When correlations are performed on the ranked absolute

concentrations of model output (Table 4-5), the source term (factor 1 containing mostly

CT) is positively correlated with temperature and is negatively correlated with DO and

ferric iron. The second source term (factor 2, CF) is not correlated with any ancillary

parameter. The dechlorination term (factor 3, 1:3 CF:DCM) is negatively correlated with

pH.

Correlations performed on the *relative* concentration of each factor in each sample were

more helpful (Table 4-5): the source term (factor 1) is positively correlated with TOC and

temperature and negatively correlated with ferric iron and DO. The second source term

(factor 2) term is not correlated with any ancillary parameter. Lastly, the dechlorination

term is and negatively correlated with redox, TOC and pH. Thus the correlations

performed on *relative* and absolute concentrations of the PMF factors do not reveal

useful information about what conditions dechlorination occurs due to the lack of

available ancillary data for this dataset.

4.4 Discussion & Implications

Analysis of the chlorinated methane dataset provided indications of degradation via microbial dechlorination in the subsurface. PMF analysis of the chlorinated methane groundwater monitoring data resolved the heterogeneous dataset into three factors representing two parent contaminants and one extent of dechlorination. The PMF model output can also be used to estimate how much of the mass of these compounds comes from dechlorination versus how much is attributable to other sources, such as use on site. The solution indicates that nearly all of the dichloromethane in the subsurface is attributable to dechlorination. Unfortunately there was insufficient data to discern which environmental conditions favor dechlorination of chlorinated methanes onsite.

The fact that the PMF output reveals at least some hint that microbial dechlorination is occurring in the subsurface addresses the final objective (goal D) of the work. However, both the PMF results and the raw data revealed few relevant correlations with ancillary parameters, making it difficult to tell a coherent story about the conditions in the subsurface that might favor microbial dehalogenation of chloromethanes. This relative failure may be due to several factors, including:

1. Not enough measurements of halomethanes

2. Too many non-detect values among those measurements

3. Extremely limited data on ancillary parameters

4. Volatility/evaporation of analytes

5. Halomethane contaminated limited to one relatively small portion of the Chambers Works facility

Of these explanations, we speculate that the most important factor was the limited measurements of ancillary parameters. The PMF program was able to converge on a meaningful solution, suggesting that flaws 1 and 2 were not fatal. However, it is possible that a larger PMF input (i.e. more measurements and more detections of halomethanes) might have resulting in a different PMF solution, especially if that extra data would have allowed the inclusion of analytes such as chloromethane and methane into the concentration matrix.
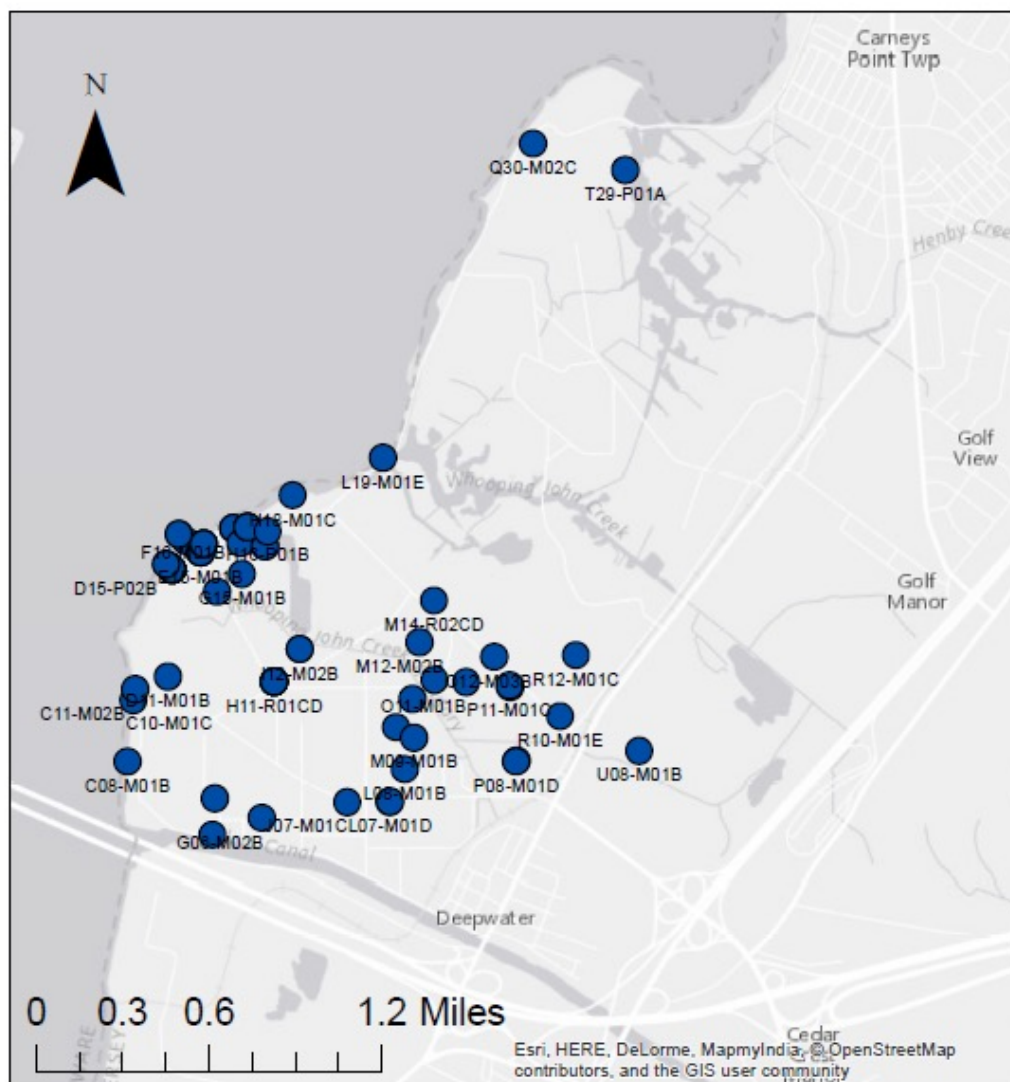
Figure 4-1. Satellite image of the site displaying the layout of the monitoring wells (blue dots) considered in the PMF2 investigation of the halomethane groundwater dataset.
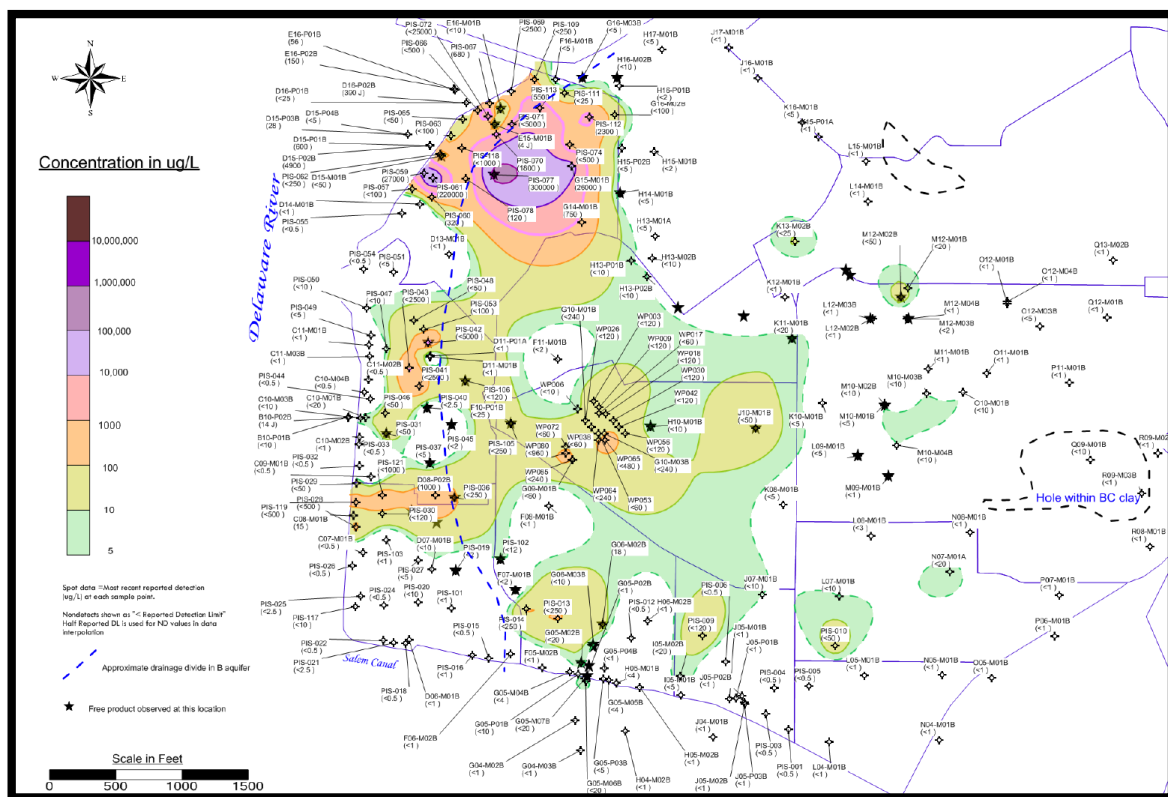
Figure 4- 2. Groundwater plume of the CT located measured in the B-aquifer onsite. Maps prepared by URS on September 19, 2011 for an internal investigation report.[27]
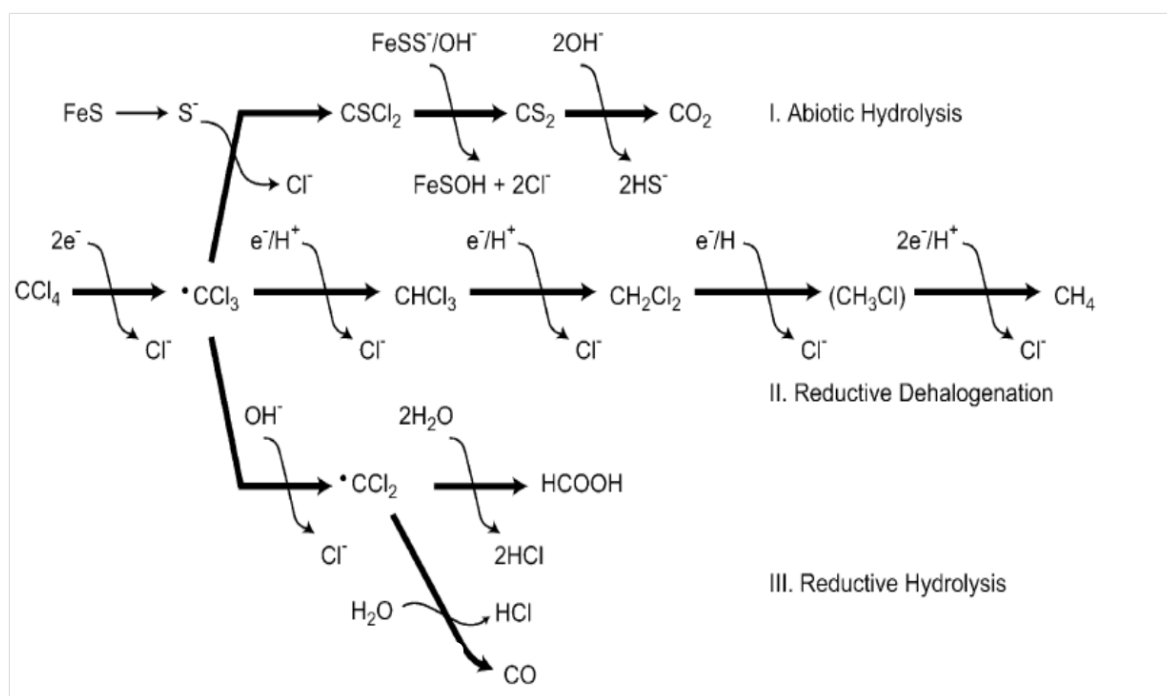
Figure 4-3. Degradation pathways of CT in the subsurface. [1]
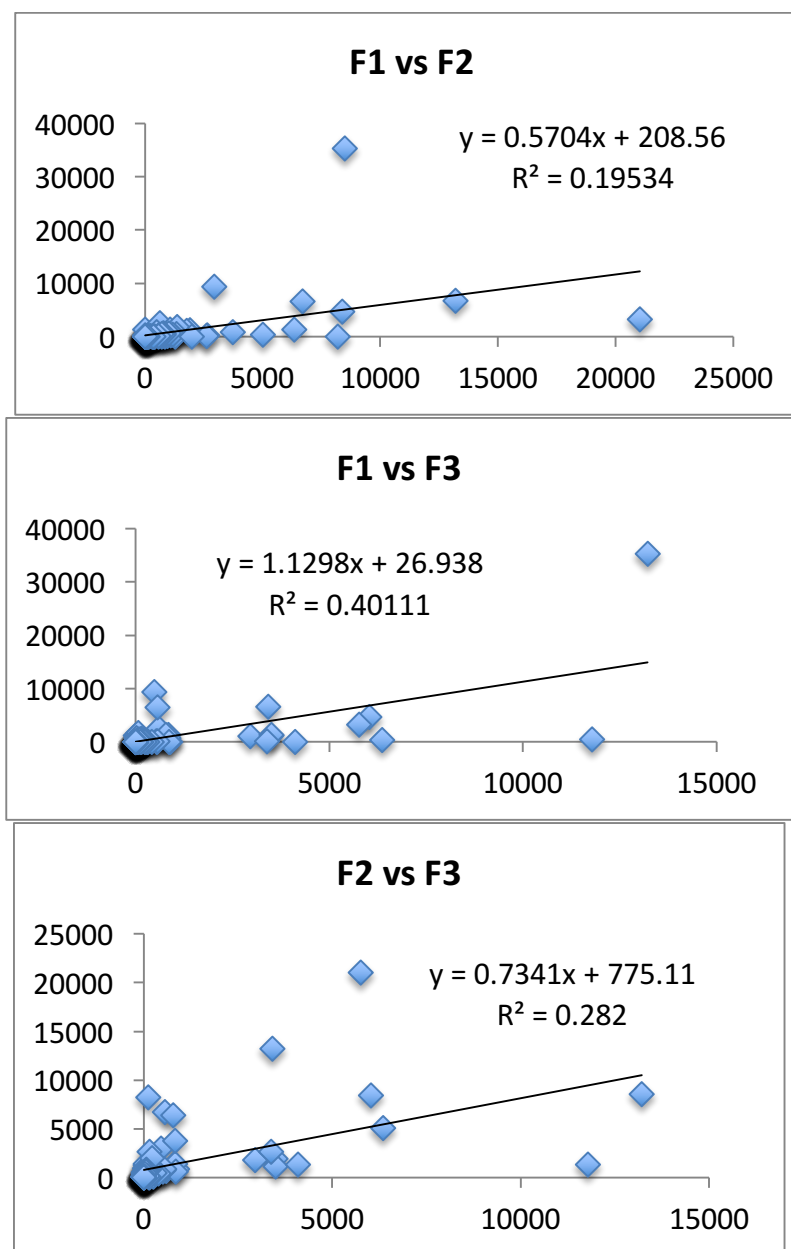
Figure 4-4. G-space plots: pair-wise comparison of the factors for the 3-factor PMF solution. When factors are independent of each other, there should be no correlation between the X and Y of each plot. The plots show a wide scatter of point with many points on and near the X-axis and Y-axis, indicating that the factors are independent of each other and rotation of the data matrix is not required.
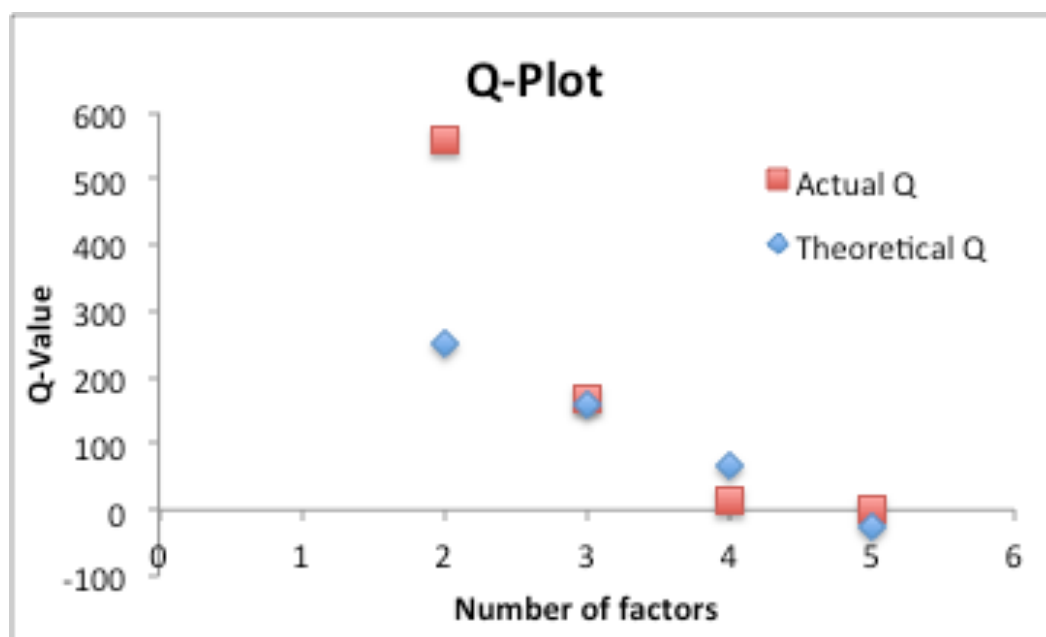
Figure 4-5. Theoretical and calculated Q-values versus the number of factors submitted to the PMF model indicating model convergence on the 3-factor PMF solution.
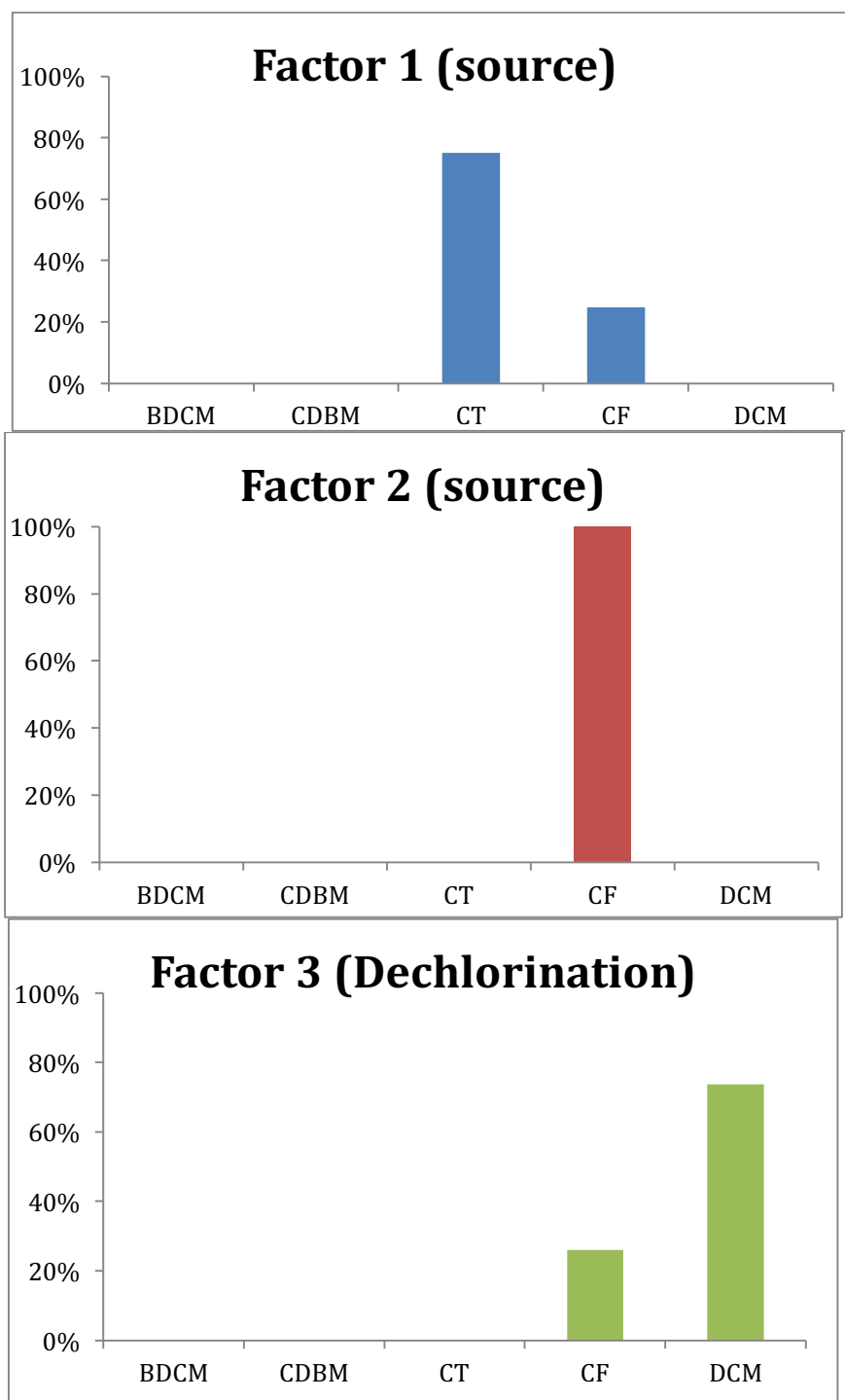
Figure 4-6. Source profiles (fingerprints) of the 3-factors generated by PMF modeling. Percentages indicate the contribution of each analyte to the factor model.
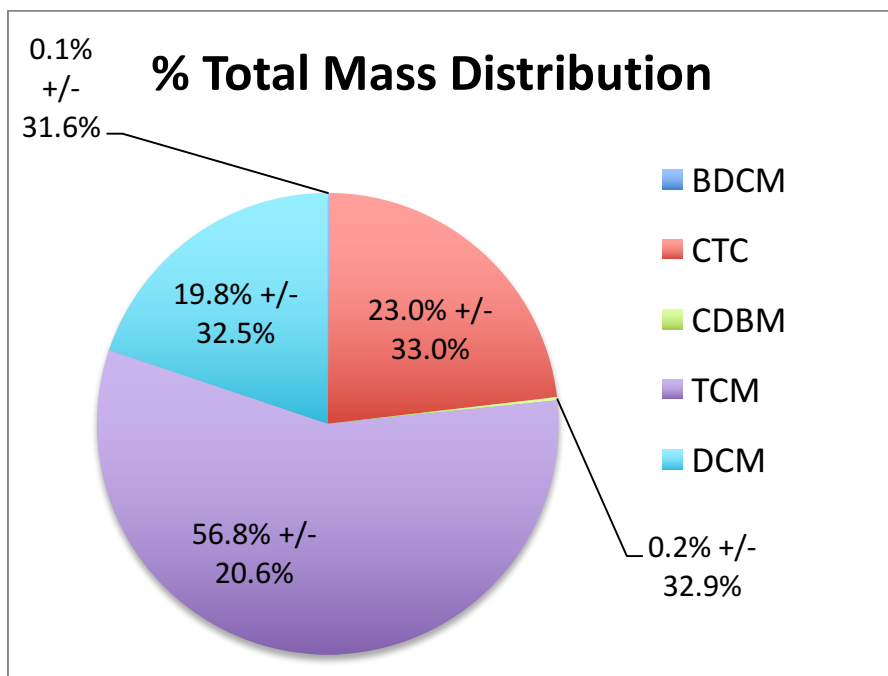
Figure 4-7. The percent (%) of total mass in the dataset that each analyte represents for the PMF2 model. The standard error is indicated in parenthesis.
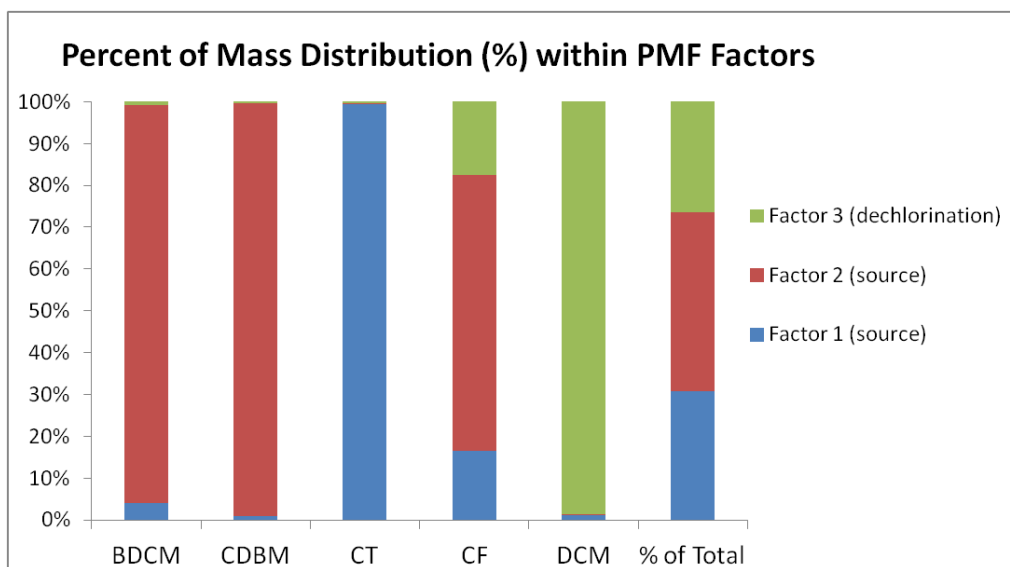
Figure 4-8. The percent (%) of total mass distribution of each analyte throughout the resolved source profiles.
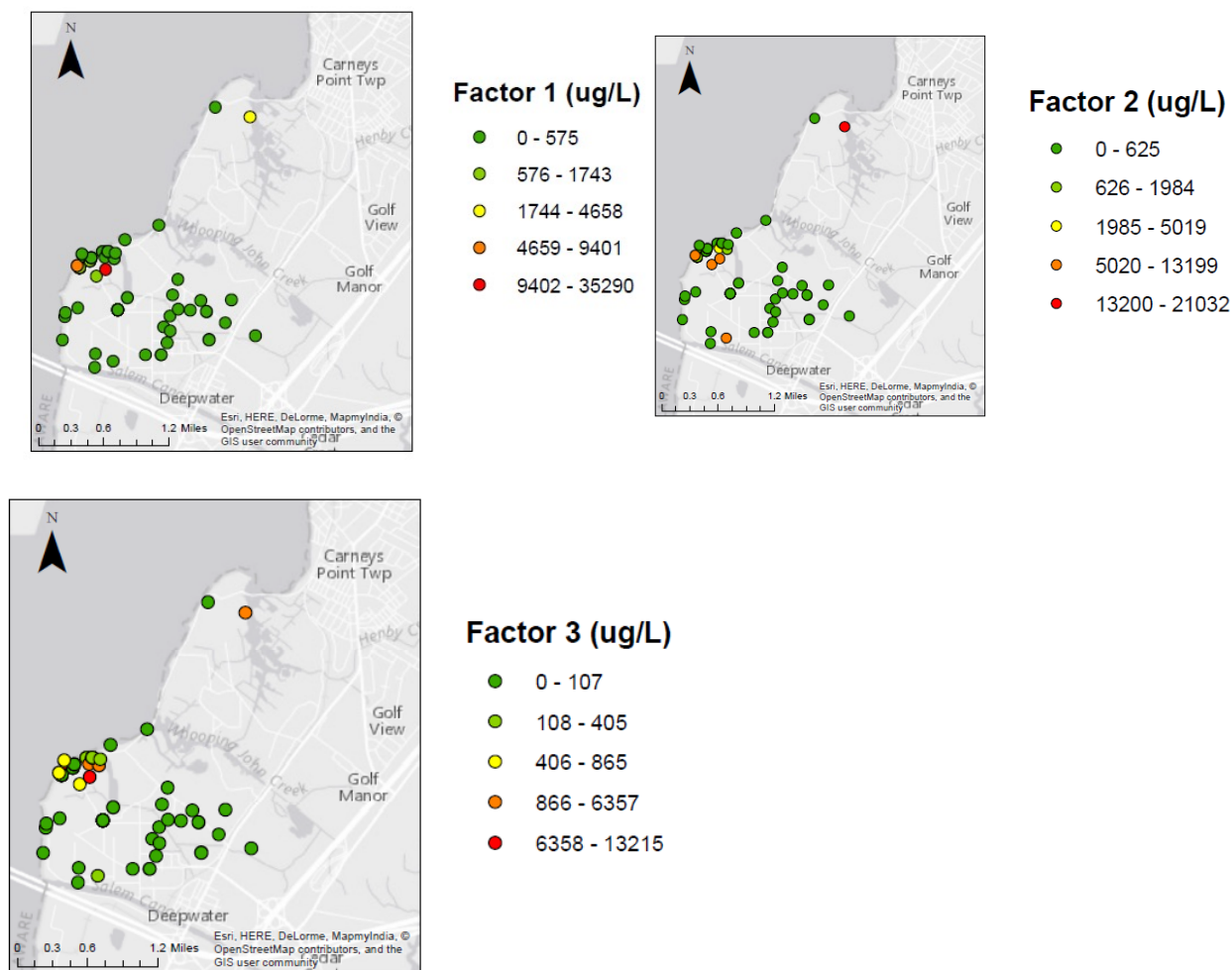
Figure 4-9. The average absolute concentration (ug/L) of each factor profile in wells throughout all years considered (1990- 2011) (factor 1 = source, factor 2 = source, and factor 3 = dechlorination). The scale for the legend was set up in percentiles (e.g., 20th, 40th, 60th, 80th, and 99th).
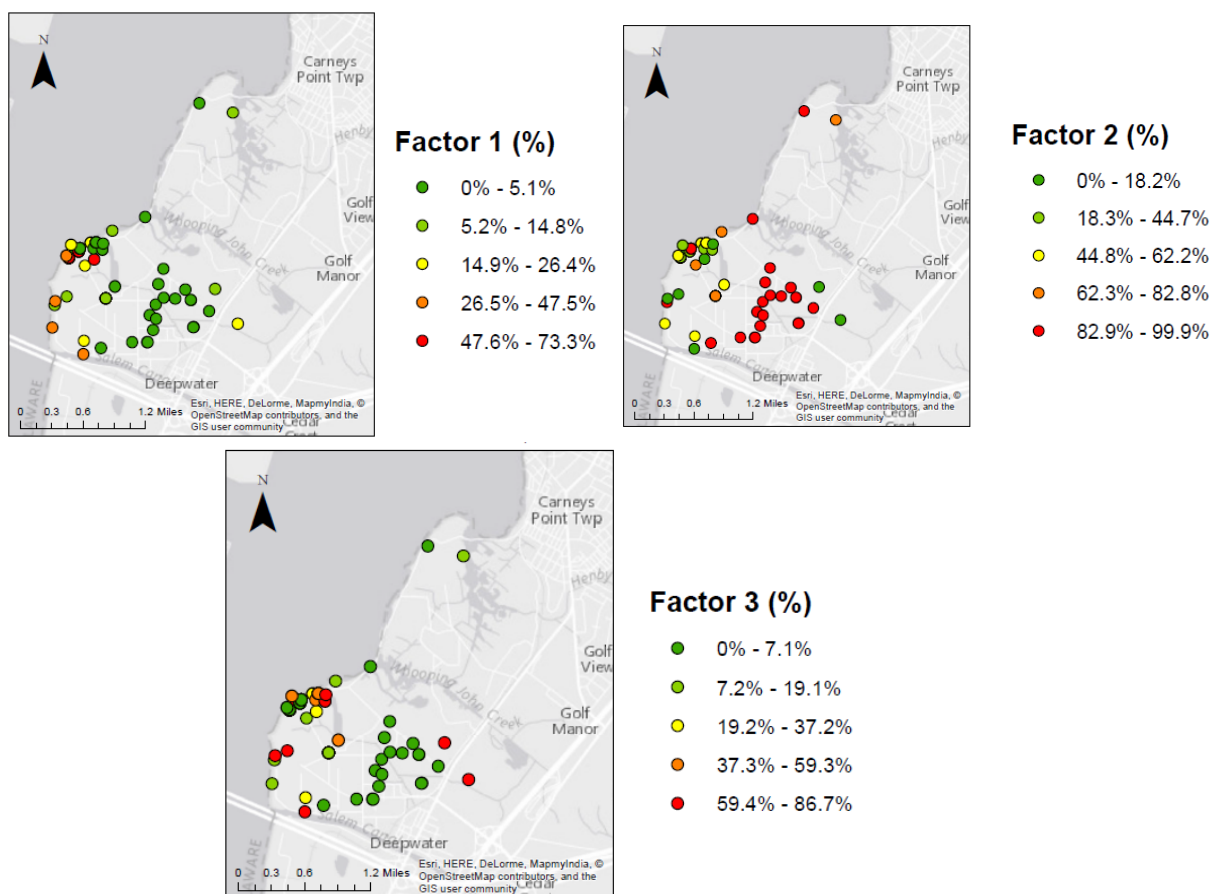
Figure 4-10. The percent of the total mass contribution (*relative* concentrations of the G-matrix) of each factor in each well is displayed throughout the study period (1990- 2011) (factor 1 = source, factor 2 = source, and factor 3 = dechlorination). The scale for the legend was set up in percentiles (e.g., 20th, 40th, 60th, 80th, and 99th).
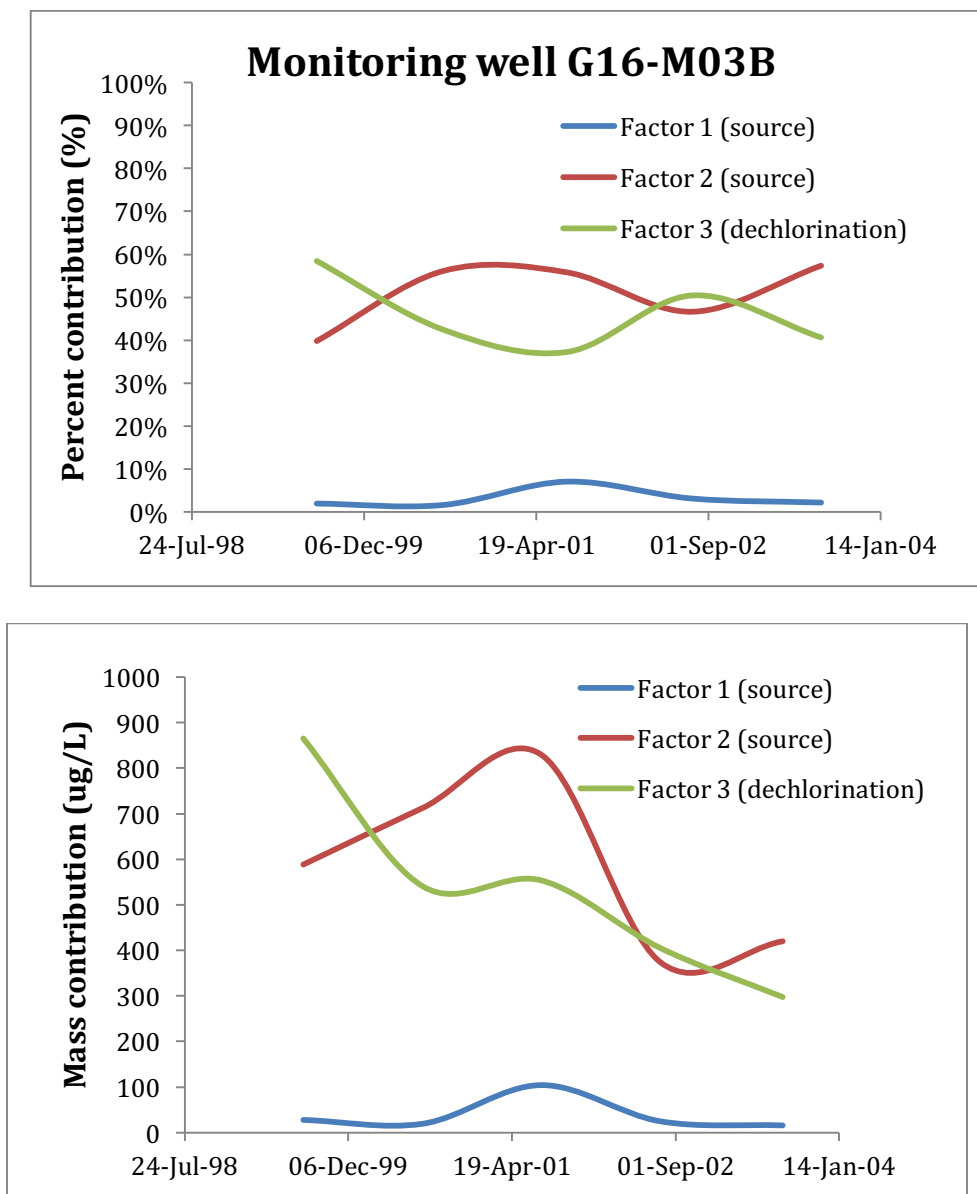
Figure 4-11. Plot of the absolute concentration (μg/L) and *relative* concentration (% of total mass) of the mass contribution (G-matrix) of the model output in well G16-M03B between the years 1999 and 2011.
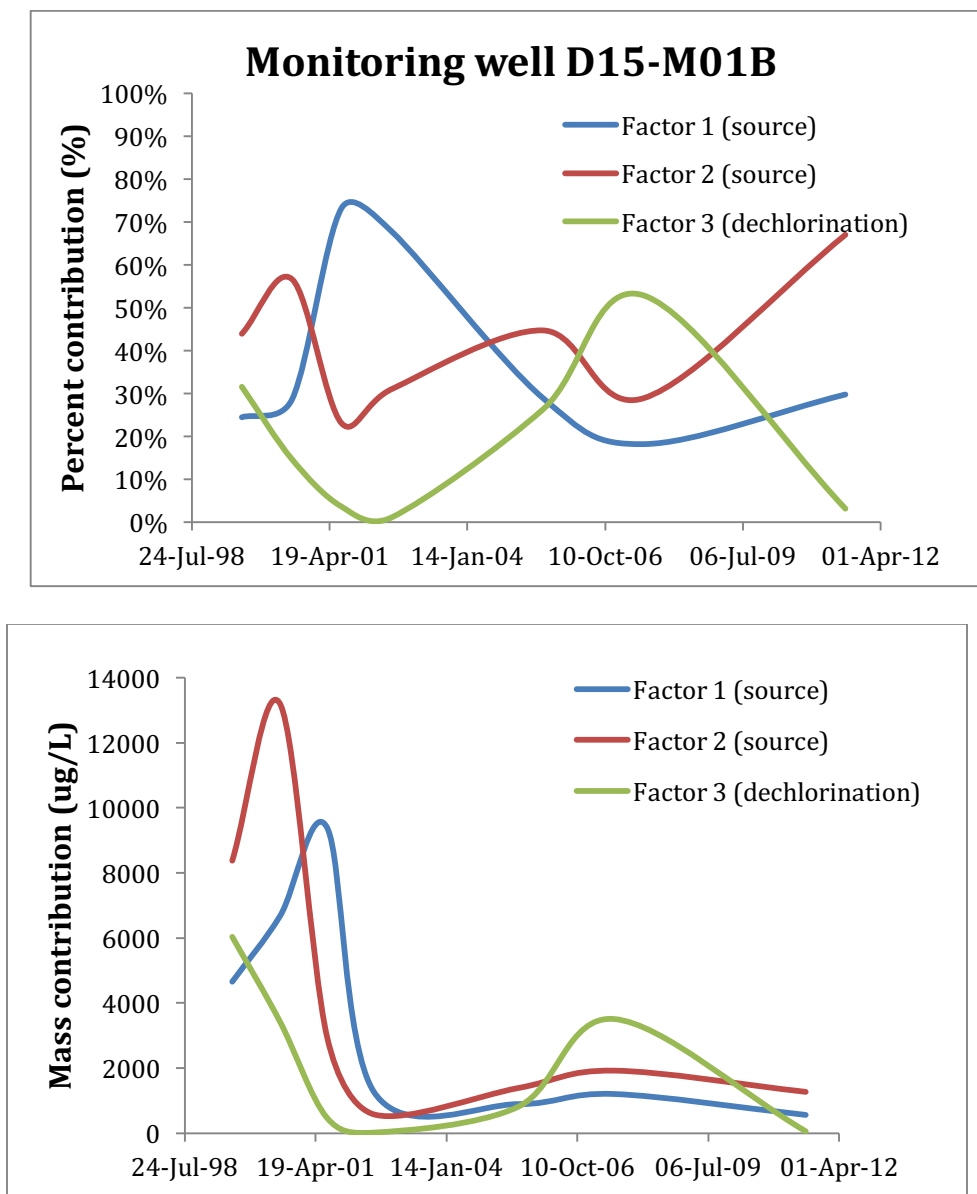
Figure 4-12. Plot of the absolute concentration (μg/L) and *relative* concentration (% of total mass) of the mass contribution (G-matrix) of the model output in well D15-M01B between the years 1999 and 2003.
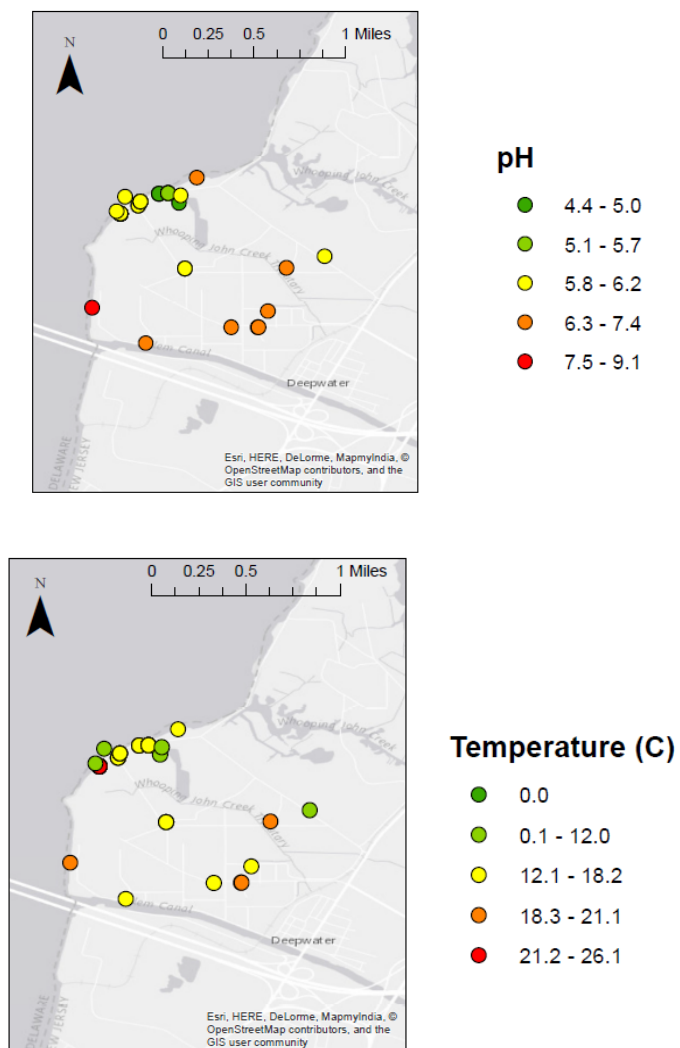
Figure 4-13. **Average temperatures (ºC) and total pH in monitoring wells considered in the halomethane factor analysis solution.**
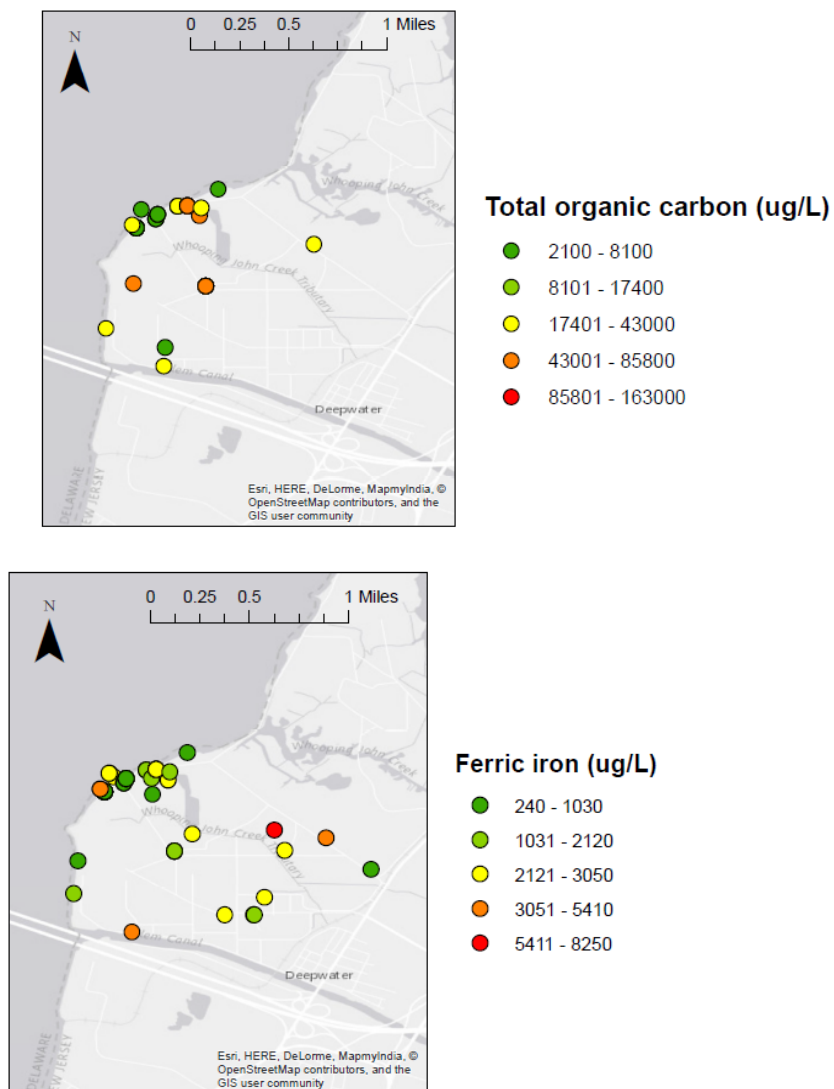
Figure 4-14. Average ferric iron (μg/L) and dissolved oxygen (DO, μg/L) and total organic carbon (TOC, μg/L) in monitoring wells considered in the halomethane factor analysis solution.

Table 4-1. The 5 halomethanes included in the PMF investigation and their molecular weight, octanol-water partitioning coefficient, LogK$_{ow}$, Henry law constant, K$_H$, and chemical structures. MW, log K$_{ow}$, and K$_H$ values obtained from U.S. EPA KOWWIN software version 1.67.
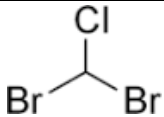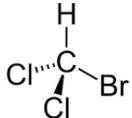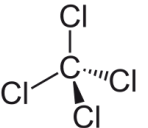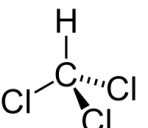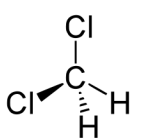
Chemical Name	MW	Log K$_{ow}$	Henry's Law Constant K$_H$ at 25°C (atm*m^3/mole)	Chemical Structure
Dibromochloromethane (DBCM)	208.28	1.70	7.83x10^{-4}	
Bromodichloromethane (BDCM)	163.80	1.61	2.12x10^{-3}	
Tetrachloromethane aka Carbon tetrachloride (CT)	153.81	2.44	2.76x10^{-2}	
Trichloromethane aka Chloroform (CF)	119.37	1.52	3.67x10^{-3}	
Methylene chloride aka Dichloromethane (DCM)	62.50	1.34	3.25x10^{-3}	

Table 4-2.   Distribution of halomethanes and ancillary concentration data regarding each analyte included in the PMF model.   Halomethanes concentrations are from from 87 aqueous groundwater samples extracted from 52 monitoring wells.   The 10th, 50th, and 90th percentile concentrations (the Xth percentile concentration is that for which X% of the measured concentrations were lower) are reported for each analyte after preprocessing the data matrix for PMF analysis.

	10th %ile	50th %ile	90th %ile	Minimum detected conc.	Maximum detected conc.	Mean
Alkalinity (µg/L)	9,077	43,000	121,300	105	400,000	74,489.9
Nitrate (µg/L)	149	1,900	5,130	48	8,100	2,379.2
TOC (µg/L)	4,506	16,900	78,730	2,100	163,000	32,699.6
Ferric iron (µg/L)	512	1,950	3,772	240	8,250	2,191.6
Sulfide (µg/L)	22,000	62,300	593,000	3,900	1,880,000	216,123.8
Temperature (ºC)	11.0	18.2	21.8	9.0	26.1	17.8
DO (µg/L)	500	1,910	3,580	420	8,250	2,080.0
pH	5.35	6.01	6.48	4.4	9.12	6.0
redox (mV)	-122.0	16.6	160.6	-175.3	275.3	16.4
Aniline (µg/L)	14.8	280	2,900	1	59,000	2,092.9
Nitrobenzene (µg/L)	4.7	265	37,100	1	99,000	9,827.5
BDCM (µg/L)	0.8	5	23.8	0.8	82	9.6
CDBM (µg/L)	0.8	3	16	0.8	77	6.6
CT (µg/L)	1	33	1,000	0.8	26,000	759.1
CF (µg/L)	16	410	4,860	1	24,000	1,919.2
DCM (µg/L)	1	52	2,540	0.8	9,600	651.1

Table 4-3. Spearman's Rank-Order Correlations for measured halomethanes: the rank of absolute concentration [C] and the rank of percent of total mass (%) of each factor versus the rank of ancillary parameters after preprocessing the data matrix for PMF analysis. For those significant trends where p < 0.05, pink sign indicates a positive correlation, light blue indicates a negative correlation and no correlation are reported as yellow. For those significant trends where p < 0.005, red indicates a positive correlations and dark blue indicates a negative correlation and no correlation is reported as yellow. Note the units of ancillary parameters are ug/L except for T (C), pH, pE, and %AN, which are unitless.

parameter	n	BDCM [C]	BDCM %	CDBM [C]	CDBM %	CT [C]	CT %	CF [C]	CF %	DCM [C]	DCM %
DO	41	yellow	pink	yellow	pink	dark blue	dark blue	yellow	yellow	yellow	yellow
Redox, Eh	35	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow
%AN	53	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow
Nitrate	14	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow
Ferric Fe	55	pink	yellow	yellow	yellow	light blue	dark blue	yellow	yellow	yellow	yellow
Sulfide	21	yellow	yellow	yellow	yellow	yellow	yellow	pink	yellow	yellow	yellow
Alkalinity	14	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow
TOC	48	yellow	yellow	yellow	yellow	yellow	dark blue	yellow	yellow	yellow	red
pH	41	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	dark blue
Temperature	41	yellow	red	yellow	pink	pink	red	yellow	yellow	dark blue	dark blue

Table 4-4. The relative standard deviation (RSD) of the G-matrix for model outputs requesting different numbers of factors, RSD of 10 model runs with random seed values.

Number of Factors	RSD of G Matrix (%)
2	0.6%
3	1.8%
4	2.1%
5	6.5%

Table 4-5. Spearman's Rank-Order Correlations on model output: the rank of absolute concentration and percent of total mass of each factor versus the rank of ancillary parameters after preprocessing the data matrix for PMF analysis. For those significant trends where $p < 0.05$, pink sign indicates a positive correlation, light blue indicates a negative correlation and no correlation are reported as yellow. For those significant trends where $p < 0.005$, red indicates a positive correlations and dark blue indicates a negative correlation and no correlation is reported as yellow. Note the units of ancillary parameters are ug/L except for T (C), pH, pE, and %AN.

parameter	n	Factor 1 (source) [C]	Factor 1 (source) %	Factor 2 (source) [C]	Factor 2 (source) %	Factor 3 (dechlorination) [C]	Factor 3 (dechlorination) %
Redox (Eh)	35	yellow	yellow	yellow	yellow	yellow	dark blue
%AN	53	yellow	yellow	yellow	yellow	yellow	yellow
DO	41	light blue	dark blue	yellow	yellow	yellow	yellow
Ferric Fe	55	light blue	dark blue	yellow	yellow	yellow	yellow
Nitrate	14	yellow	yellow	yellow	yellow	yellow	yellow
Sulfide	22	yellow	yellow	yellow	yellow	yellow	yellow
Alkalinity	14	yellow	yellow	yellow	yellow	yellow	yellow
TOC	76	yellow	red	yellow	yellow	yellow	dark blue
pH	41	yellow	yellow	yellow	yellow	dark blue	dark blue
Temperature	41	pink	red	yellow	yellow	yellow	yellow

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Chapter 5: Conclusions

5.1 Summary of Findings

This dissertation presented source apportionment of various classes of chlorinated organic solvents in the groundwater at the Chambers Works facility located in Deepwater, New Jersey. The main goal of this study was to better understand how, when, and under which conditions do the different classes of chlorinated solvents undergo dechlorination in the subsurface.

Source apportionment using PMF was used to identify sources of chlorinated benzenes in the groundwater at Chambers Works. PMF analysis revealed three resolved factors, one factor representing a source of chlorinated benzenes and two representing dechlorination products. Of the two dechlorination factors, one represented a more advanced stage of dechlornation than the next. The advanced dechlorination factor is correlated with highly-reducing conditions, typical of methanogenic conditions. This is the largest dataset, which is comprised of 597 aqueous groundwater samples in which only 12% are below the limit of detection (BDL). PMF clearly resolved the three factor solution for the chlorinated benzene dataset.

As with the chlorinated benzene dataset, we found two dechlorination factors in the chlorinated ethene dataset. A total of 76 aqueous groundwater samples, in which 37% of the analyte measurements were BDL, were applied to the PMF model and three factors were resolved. One factor represented a source of parent compound and two represented

different stages of dechlorination, in which one stage was more advanced than the other. In this case the partial dechlorination factor was correlated with lesser-reducing conditions representative of sulfate-reducing conditions whereas the advanced dechlorination factor was correlated with highly-reducing conditions typical of methanogenesis.

Finally, the chlorinated methane dataset consisted of 87 aqueous groundwater samples in which a total of 42% of the measurements were BDL. Just like the chlorinated benzene and chlorinated ethene dataset, the PMF model resolved three factors. Of the three factors, two represent sources of parent compound and one indicates dechlorination of chlorinate methanes. The model results, however, are not clear between the three and four factor solutions and there was not enough information regarding ancillary measurements to correlate results with and to discern the environmental conditions in which dechlorination of chlorinated methanes is occurring in the subsurface.

5.2 Implications and Future Work

In Chapter 1 of this dissertation, we asked a series of questions regarding the applicability of our approach to groundwater monitoring data:

1. Can PMF analysis be successfully performed on data of this quality?
2. Can PMF analysis indicate where, when and under what conditions microbial dechlorination of contaminants is occurring in the groundwater at Chambers Works?

3. Can the answers to question 2 indicate any practical approaches that the operators of Chambers Works could use to enhance the natural dechlorination occurring at their site?

4. What can this data mining exercise tell us about the quantity and quality of data needed to answer questions 1 through 3? Can we make recommendations about how data collection and management should be conducted in the future to aid data mining efforts?

Question 1: Can PMF analysis be successfully performed on data of this quality?

Yes, PMF analysis is useful in interpreting groundwater data. For all three data sets, the PMF analysis did converge on a stable solution that provided insights into the processes occurring in the subsurface. Even a data set with just 87 aqueous groundwater samples in which a total of 42% of the measurements were BDL was sufficient for this purpose. The chromatographic effect and the lack of mixing in the subsurface did not seem to have noticeable effects on the PMF solutions. More information about reproducibility of the analytical methods would have aided the construction of the PMF inputs. In addition, it would be highly beneficial to measure all analytes in all samples, and to use detection limits that allow even low concentrations to be detected. From more of a monitoring standpoint of environmental compliance, non-detects are a good thing since this indicates that contaminants of concern are not present at detectable levels, but not if the results are to be used for data mining purposes. It would also be helpful to measure degradation

products, even when they are not regulated groundwater contaminants. Of course, analytical measurements are expensive this is not likely to be feasible in every case.

Question 2: Can PMF analysis indicate where, when and under what conditions microbial dechlorination of contaminants is occurring in the groundwater at Chambers Works?

Yes, provided enough data on ancillary parameters that are indicative of redox conditions in the subsurface, correlating the PMF output with those parameters can suggest the conditions that are conducive to dechlorination. As noted above, more data is always better, and it is highly beneficial to measure all analytes, including redox indicators, in all samples. The novel redox indicator used in this dissertation, aniline as a percent of aniline+nitrobenzene (%AN) significantly enhanced our ability to interpret the PMF results. Most importantly, correlation of the ancillary parameters with the PMF output provided a more coherent narrative than correlations with the raw data, suggesting that factor analysis does add value to the data mining exercise.

Question 3: Can the answers to question 2 indicate any practical approaches that the operators of Chambers Works could use to enhance the natural dechlorination occurring at their site?

Yes. For the chlorinated benzenes and ethenes, the PMF approach was able to indicate when and where microbial dechlorination of each class of contaminant occurred in the

groundwater at Chambers Works. PMF was also capable of indicating what conditions

dehclorination of chlorinated benzenes and chlorinated ethenes occurred. In the case of

the chlorinated methane dataset, there was not sufficient supportive information to

discern which conditions favored dechlorination. In the case of the chlorinated benzene

and chlorinated ethene solutions, the advanced dechlorination regimes were correlated

with highly methanogenic conditions indicating that advanced dechlorination favors

highly reducing environments. Enhanced natural attenuation would therefore benefit

from attempts to drive the redox conditions toward reducing environment in order to

achieve complete dechlorination. For the chlorinated benzenes, this approach would

yield benzene, which is more easily degrade via aerobic mechanisms. It is also soluble

and more likely to be intercepted by pumping wells and then transferred to the onsite

wastewater treatment plant. There is can undergo aerobic degradation and also volatilize.

Question 4: What can this data mining exercise tell us about the quantity and quality of data needed to answer questions 1 through 3? Can we make recommendations about how data collection and management should be conducted in the future to aid data mining efforts?

The data mining approach works best with a relatively cohesive dataset. In the best case

scenario this would be one that measures all contaminants in all samples at the same time

using the same or similar methods (those with similar MDLs) that report surrogate

recoveries. In additions measuring all possible degradation products would be helpful. It

appears that 70 or so samples *in which all or most analytes were measured* was enough to provide useful results by the data mining approach for this location.

In summary, the data mining approach utilizing a factor analysis tool such as PMF can be a powerful tool for understanding when, where, and why microbial dehalogenation of halogenated solvents occurs in groundwater.

For future work we recommend the following regarding data collection and management: 1) measure all possible degradation products (aerobic and anaerobic mechanisms), 2) report all quality assurance criteria including field and laboratory surrogate recoveries 3) measure analytes using the same (or similar) analytical methods and 4) measure all the contaminants and redox indicators in the same sample at the same time.