

# Long-Term Fate of an Emplaced Coal Tar Creosote Source

by

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A thesis  
presented to the University of Waterloo  
in fulfillment of the  
thesis requirement for the degree of  
Master of Science  
in  
Earth Sciences

Waterloo, Ontario, Canada, 2007

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## **AUTHOR'S DECLARATION**

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

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## Abstract

An emplaced source of coal tar creosote within the sandy Borden research aquifer has provided an opportunity to document the long term (5140 days) natural attenuation for this complex mixture. Plumes of dissolved chemicals were produced by the essentially horizontal groundwater flowing at about 9 cm/day. Eleven chemicals were extensively sampled seven times using a monitoring network of ~280 14-point multilevel samplers.

A model of source dissolution using Raoult's Law adequately predicted the dissolution of nine of eleven compounds analysed. Mass transformation has limited the extent of the plumes as groundwater flowed more than 500 m yet the plumes are no longer than 50 m. Phenol and xylenes were removed and naphthalene was attenuated from its maximum extent on day 1357. Some compound plumes reached an apparent steady state and the plumes of other compounds (dibenzofuran and phenanthrene) are expected to continue to expand due to an increasing mass flux and limited degradation potential.

Biotransformation is the major process controlling natural attenuation at the site. The greatest organic mass loss is associated with the high solubility compounds. However, the majority of the mass loss for most compounds has occurred in the source zone. Oxygen is the main electron acceptor yet the amount of organics lost cannot be accounted for by aerobic mineralization or partial mineralization alone.

After 10 years the source zone was treated with permanganate *in situ* to reduce the flux of contaminants into the dissolved plume and to permit natural attenuation to further reduce the plume extent. A sufficient mass of permanganate was injected to oxidize ~10% of the residual source. Laboratory experiments demonstrated that eight of ten of the study compounds were readily oxidized by permanganate. Once treated oxidized compounds displayed a reduced plume mass and mass discharge while they migrated through the monitoring network. Once beyond the monitoring network the mass discharge and plume mass of these compounds returned to pre-treatment trends. Non-reactive compounds displayed no significant decrease in mass discharge or plume mass. Overall the partial *in situ*

chemical oxidation of the coal tar creosote source produced no long-term effect on the dissolved plumes emanating from the source.

## Acknowledgements

I would like to thank Dr. Jim Barker, my supervisor, who has been a mentor throughout my post-secondary education. His guidance, knowledge and humour have made this sometimes difficult process much more enjoyable. I also would like to thank the members of my committee Carol Ptacek and Neil Thomson for their time and thorough review of the work.

I have much gratitude towards Conestoga Rovers & Associates who assisted in funding this research and to Mike Matayk and Jody Vaillancourt who were my liaisons.

For the countless number of samples sent to the Organic Geochemistry Lab I would like to thank Marianne VanderGriendt and Shirley Chatten.

I am grateful for the people who made the trek to Borden and assisted in sampling the field site, Sharon Joseph, Jenn Mahoney, Claudia Naas, Erika Williams and many co-op students over the years.

I appreciate Wayne Noble's assistance in using the HPLC and entertaining my random questions about organic acids.

The toxicology testing would not have been possible without Erika Williams' expertise and the generous use of the labs at Stantec.

Two other people I would like to acknowledge are Barb Butler and Rob McLaren, who tolerated my random appearances at their office with haphazard questions.

Finally, I would like to thank my family for the support they have provided in everything I have ever done.

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# Chapter 1

## Overview

Coal tar and coal tar creosote are significant sources of persistent groundwater contamination. This complex mixture of aromatic, heteroaromatic and phenolic compounds are common waste products in the petroleum coal and wood preserving industries. When coal tar enters the subsurface a number of overlapping individual dissolved compound plumes are produced due to the different solubilities and sorptive properties of the compounds. Natural attenuation processes such as sorptive retardation and biodegradation may restrict the extent of these plumes.

In 1991 a coal tar creosote residual source NAPL was emplaced below the water table within the sandy research aquifer of CFB Borden. This long term study was undertaken to assess the behaviour of coal tar organic compounds in groundwater under controlled conditions. The installation of the source was completed by Malcolmson (1992) with the following 3.7 years of plume development and attenuation monitored by King (1997). The creosote source site has been the subject of numerous investigations which examined some aspect of the source, and/or plumes from toxicology (Maude, 1996), computer modeling (Martin, 2004), remediation studies (Lauzon, 1998; Lamarche, 2002) and organic and/or inorganic sampling and data analysis (Blaine, 2000; Martin, 2002; Fraser, 2005; Joseph, 2006).

After 10 years of monitoring the coal tar creosote plume the source zone was flushed with permanganate to oxidize the residual (Lamarche, 2002). There are numerous NAPL source zone remedial technologies however none are likely to remove all the NAPL. As a result the focus of NAPL source zone remediation is changing to reducing contaminant flux into the plume so that natural attenuation processes can provide reliable protection to the receptors. Unfortunately assessing the extent of such remedial success is not standardized and often not credible. Thus the research intended to evaluate the benefit of partial NAPL source zone remediation from the perspective of reducing the flux of contaminants into the dissolved plume and permitting natural attenuation to further reduce the plume extent. The application of the source zone

oxidation and the short term effects on the creosote source were conducted by Lamarche (2002) in 2000.

The focus of the current study is to assess the state of the coal tar creosote plumes by examining the extent of natural attenuation and the long-term impact the source oxidation had on the dissolved plumes. This thesis was written as two papers each of which has been submitted for publication (Fraser et al., in submission; Thomson et al., in submission). Chapter 2 examines the extent of natural attenuation of the coal tar creosote plume. This is the first in depth examination of the plume to incorporate a qualitative assessment of the plumes, a mass balance and attempt to understand biotransformation processes controlling natural attenuation at the site since King (1997). Chapter 3 examines the impact of the source zone oxidation on the flux of contaminants and state of the dissolved plumes over the long term. Conclusions and recommendations of the research are found in Chapter 4 and Chapter 5.

## **Chapter 2**

### **Natural Attenuation of a Plume from an Emplaced Coal Tar Creosote Source Over 14 Years**

Coal tar creosote is a complex mixture of polycyclic aromatic hydrocarbons (PAH's), N- S- and O- heterocyclic hydrocarbons and phenolic compounds. This dense non-aqueous phase liquid can contain upwards of 200 compounds (Mueller et al., 1989). Coal tar creosote is a common waste product in the coal gasification and wood preserving industry and can enter the subsurface through spills and historic waste disposal practices. When creosote enters the subsurface a number of overlapping individual compound plumes are produced due to the different solubilities and sorptive properties of these compounds. This complex mixture poses a long term source of groundwater contamination due to the slow dissolution of many compounds. Natural attenuation processes such as sorptive retardation and biodegradation may restrict the extent of these plumes (Barker et al., 2005).

Monitored natural attenuation (MNA) is a widely used practice to deal with creosote contaminated sites due to the large costs and minimal benefits of active remedial technologies such as pump and treat (Bockelmann et al., 2003; Brenner et al., 2002; Logan et al., 1999). Natural attenuation of creosote occurs as a result of a number of processes including dispersive dilution, sorption and biotransformation. This last process is dependent on factors such as aeration, nutrient supplementation as well as the capability of the microbial population (King et al., 1999).

Although the chemical composition varies with each individual coal tar creosote NAPL, often the principal compounds are PAH's with naphthalene being the most abundant (Ghoshal et al., 1996; Mueller et al., 1989). When coal tar creosote dissolution occurs in groundwater it is governed by the solubility of compounds as well as their mole fractions in the NAPL. Thus aqueous concentrations are usually greatest for compounds such as naphthalene (high solubility and high mole fraction) as well as phenols (extremely high solubilities and moderate mole fractions). Over time when these abundant, soluble compounds have been leached from the source other less soluble

compounds can become prominent in the groundwater. At a charcoal manufacturing waste site in Michigan Klecka et al. (1990) found that the principal aqueous constituents were phenols and naphthalene with naphthalene detected at concentrations an order of magnitude greater than other PAH's. Kiilerich & Arvin (1996) examined data from 44 waste sites contaminated with creosote and found that high aqueous concentrations of naphthalene (11 000 to 19 000 µg/L) and phenol (39 000 to 660 000 µg/L); as well benzene and xylenes were common. Bianchin et al. (2006) examined creosote-derived contamination transported by anaerobic groundwater beside the Fraser River in British Columbia, Canada. Naphthalene accounted for more than 90% of the creosote-derived aqueous phase contamination in the plume. A gas manufacturing plant in Germany has a NAPL source zone from the former coal tar and benzene distilleries dating back well over a century (Zamfirescu & Grathwohl, 2001). Acenaphthene and benzene are the dominate contaminants. Acenaphthene is recalcitrant with concentrations at the far end of the monitoring network two orders of magnitude greater than concentrations of all other compounds detected. This recalcitrance was attributed to degradation of naphthalene, which was required to support cometabolism of acenaphthene.

King & Barker (1999) initially characterized the Borden emplaced creosote source. They found that dissolved phenol, xylenes and naphthalene plumes were the most extensive initially with phenol being leached from the NAPL 626 days into the study. By the end of the study (1357 days) the aqueous contamination was dominated by naphthalene in terms of concentration as well as extent of the plume.

The purpose of the present paper is to examine the longer-term extent of natural attenuation of a coal tar creosote plume created by a source emplaced in 1991. Processes controlling natural attenuation at the site are identified and the amount of degradation estimated. The findings for six organic compounds first presented by King & Barker (1999) are updated with sampling up to 2005, 5140 days after source emplacement. Four additional organic compounds with lower solubilities and greater sorption that hadn't developed significant plumes during the initial 3.7 year study by King & Barker (1999) are also introduced.



## 2.1 Site Description

The field site is located at Canadian Forces Base (CFB) Borden, approximately 80 km northwest of Toronto, Ontario, Canada. The research site has been extensively documented over 20 years. King & Barker (1999) summarized the aquifer properties. Hydraulic conductivity is typically  $8 \times 10^{-5}$  m/s and groundwater flow is essentially horizontal at about 9 cm/day. At a depth of approximately 9 m the unconsolidated sand grades into silts and clays.

A low organic carbon landfill leachate plume from an abandoned landfill is found at a depth of 6 to 7 m below ground surface (bgs) in the research area. The inorganic chemistry of the landfill leachate plume was examined in detail (MacFarlane et al., 1983; Nicholson et al., 1983). Groundwater from the top of this landfill leachate plume to the water table is unaffected by the landfill (King et al., 1999). This is where the current research was conducted.

In August of 1991, 74 kg of coal tar creosote was mixed with 5800 kg sand and emplaced from 2 to 3.5 m bgs in two blocks each 1.5 m deep, 2 m wide (perpendicular to horizontal groundwater flow) and 0.5 m thick. The blocks were placed 1 m apart and 0.5 to 1.5 m below the fluctuating water table. The non-aqueous phase liquid (NAPL) was mixed at less than residual concentrations so the source was not mobile. Sand coarser than Borden sand was used as the matrix in the source zone to ensure conductivity was not decreased by the addition of creosote (King & Barker, 1999).

The source was placed up gradient of an existing monitoring network that was installed in the early 1980's for a previous plume study (Mackay et al., 1986). To date the monitoring network consists of approximately 280 multilevel samplers arranged in fences perpendicular to groundwater flow and downgradient of the source. Each fence consists of between 5 to 15 wells at 0.5 to 4 m spacing with distance between fences at 2 m near the source zone and 4 m near the end of the monitoring network. Each multilevel consists of 14 vertical ports at 20 to 30 cm intervals over the depth of 1.5 to 5 m bgs. (King & Barker, 1999).

On day 2110 after source installation a funnel and gate system was installed approximately 25 m downgradient from the source (Lauzon, 1998). As a result the

behaviour of the plume past this point is affected both hydraulically and chemically. The funnel and gate remains in place to date, however, reactive material was removed before sampling day 3619 and groundwater has been allowed to flow freely through this system. Minimal mass removal was attained and therefore this remediation experiment has not significantly impacted the findings within this paper.

In the fall of 2001 (3672 to 3707 days since source emplacement) *in situ* chemical oxidation (ISCO) of the source was undertaken. Approximately 790 moles of permanganate was delivered under natural gradient conditions. Using an average stoichiometric ratio of 1:18.6 for permanganate reactivity with organic compounds suggests that about 40 moles of creosote compounds could potentially have been oxidized. At the time of treatment there were approximately 350 moles of creosote compounds remaining in the source zone. This is calculated as the total moles of creosote emplaced (74 kg with an assumed molecular weight of 150 g/mol) minus the phenols completely removed (1 kg) and soluble compounds that have been leached (based on mass discharge calculations, see section 5). Therefore the permanganate could have oxidized no more than 11% of the source. The monitoring network was sampled on two different occasions since treatment was initiated and there does not appear to be a significant impact on the dissolved plume of organic compounds. The impact of the ISCO is examined in more detail in Chapter 3.

## 2.2 Plume Sampling

The plume was sampled for a range of organic and inorganic parameters 278 (King, 1997), 626 (King, 1997), 1357 (King, 1997), 3619 (Blaine, 2000), 4315 (Fraser, 2005) and 5140 (this study) days after source installation (Appendix A). These snapshots represent a one to four week period when from 706 to 2712 points were analysed for: phenol, m-xylene, naphthalene, 1-methyl naphthalene, acenaphthene, biphenyl, phenanthrene, anthracene, dibenzofuran, fluorene and carbazole. An exception is sample day 1357 for which there is no data available for fluorine. It is assumed these compounds represent 65 weight % of the creosote mixture based on analysis of the mole fractions of these compounds during source installation. The remaining 35 weight % of the creosote compounds are assumed to be higher molecular weight compounds that are generally insoluble. In addition select points were analyzed for oxygen, nitrate, sulphate, manganese, iron (II) and methane, 1357 (King, 1997), 5140 (this study) days since source emplacement.

All organic and methane analyses were performed at the University of Waterloo Organic Geochemistry Lab using a Gas Chromatographic technique (King & Barker, 1999; Kampbell et al., 1989). Inorganic samples (sulfate, nitrate, iron, manganese) were analyzed using a HACH Spectrophotometer. Dissolved oxygen was measured in the field using a flow through cell and an Orion DO probe.

On day 5386 a composite 4 L groundwater sample was collected from sampling points 5, 6 and 7 at wells N3 (background), 9 (within plume) and 30 (in front of plume). Samples were submitted to Stantec for toxicological analysis, in particular a *Ceriodaphnia dubia* assay. Environment Canada protocol for the *C. dubia* assay was followed (Environment Canada, 1997).

Groundwater samples were also collected for analysis of Benzoic Acid on sample day 5386. Samples were collected from wells N3, 9 and 30 sampling points 5, 6, and 7 as well as a portion of the composite sample that was submitted for the *C. dubia* assay. Samples were collected in glass bottles and treated with concentrated formic acid at a rate of 5 ul to 4 ml to acidify the sodium benzoate to benzoic acid. Samples were transported to the University of Waterloo where they were centrifuged for 5 minutes prior to analysis.

A high performance liquid chromatograph (HPLC) equipped with a Zorbax SB-C18 (4.6 x 150 mm) 3.5-micron rapid resolution column was used with a mobile phase composed of 20% acetonitrile and 80% sodium acetate buffer with a pH of 4.3.

### 2.3 Source Dissolution

Raoult's Law was used to model the change in the relative concentration ratios ( $C/C_0$ ) of selected compounds in groundwater leaving the NAPL source zone. In two case studies Raven & Beck (1990) found the predicted PAH concentrations and the measured maximum PAH concentrations in groundwater conformed within a factor of two. Broholm et al. (2005) found that Raoult's Law adequately described the apparent field dissolution of a simple mixture of three chlorinated solvents. Frind et al. (1999) established that mass transfer is an equilibrium process for homogeneous DNAPL sources at Borden. King & Barker (1999) determined the Raoult's Law model was in agreement with monitoring data of the actual source leachate and that it provided a reasonable framework for qualitative prediction of trends in source leachate composition.

The current study expanded the King & Barker (1999) Raoult's Law source dissolution model to include 19 creosote compounds initially analysed by Malcolmson (1992) at the time of the source installation. The time frame was also extended to day 5140. The remaining unidentified compounds in the creosote NAPL (35 weight %) were assumed to be insoluble with a molecular weight of 150 g/mol. A groundwater flux ( $q$ ) of 0.03 m/day and a time step of 5 days, representing the time required for one source volume of groundwater to be replaced, was used over the 5140 days. The formulation of Pankow and Cherry (1996) was used:

$$C_1^i = x_1^i S_L^i = ((M_0^i - q A \Delta t C_0^i) / M_0^T) S_L^i \quad (2.1)$$

where  $C^i$  is the aqueous concentration (moles/m<sup>3</sup>) of compound  $i$ ,  $x^i$  is the mole fraction of  $i$  in the NAPL mixture and  $S_L^i$  (moles/m<sup>3</sup>) is the liquid solubility of compound  $i$ . The subscripts 0 and 1 indicate  $t=0$  and  $t=1$ ,  $M^i$  is moles of  $i$  in the NAPL phase,  $q$  is the Darcy flux through the source (m/day),  $A$  is the cross-sectional area of the source perpendicular to the direction of groundwater flow (m<sup>2</sup>) and  $M^T$  is the total moles of all compounds in the NAPL phase.

The liquid solubility of polycyclic aromatic hydrocarbons solid at field temperature is calculated as the super-cooled liquid solubility (Pankow and Cherry, 1996):

$$S_L^i = S_s^i \exp\left[6.8\left(\frac{T_M^i}{T} - 1\right)\right] \quad (2.2)$$

where  $S_s^i$  is the solid solubility,  $T_m$  is the melting point in degrees Kelvin and T is the system temperature also in degrees Kelvin.

Figure 2.1 illustrates the changing predicted mass discharge (g/day) of each compound (MD) over 5140 days, relative to the initial mass discharge of that compound ( $MD_0$ ), in the groundwater emanating from the source. The very soluble compounds, phenol, p cresol, 2,6- dimethylphenol and indole are removed within 150 days. These compounds are well represented by a single line in Figure 2.1. The rapid dissolution of these soluble compounds caused an initial increase in the mole fraction of all other compounds in the NAPL and consequently increasing MD/ $MD_0$  to well above 1.

Discharge of naphthalene, carbazole and m-xylene increases for less than 150 days and then gradually decreases. At late time m-xylene is completely removed and naphthalene and carbazole relative mass discharge is reduced to ratios less than 0.1.

Discharge of dibenzofuran, 2-methyl naphthalene, 1-methyl naphthalene, acenaphthene, biphenyl and fluorene gradually increases and then remains relatively consistent. Within 5140 days, mass discharge of these compounds also begins to decrease. The mass discharge of the relatively insoluble compounds, anthracene, phenanthrene, naphthacene, fluoranthene, chrysene and pyrene continue to increase over time as the more soluble compounds are removed.

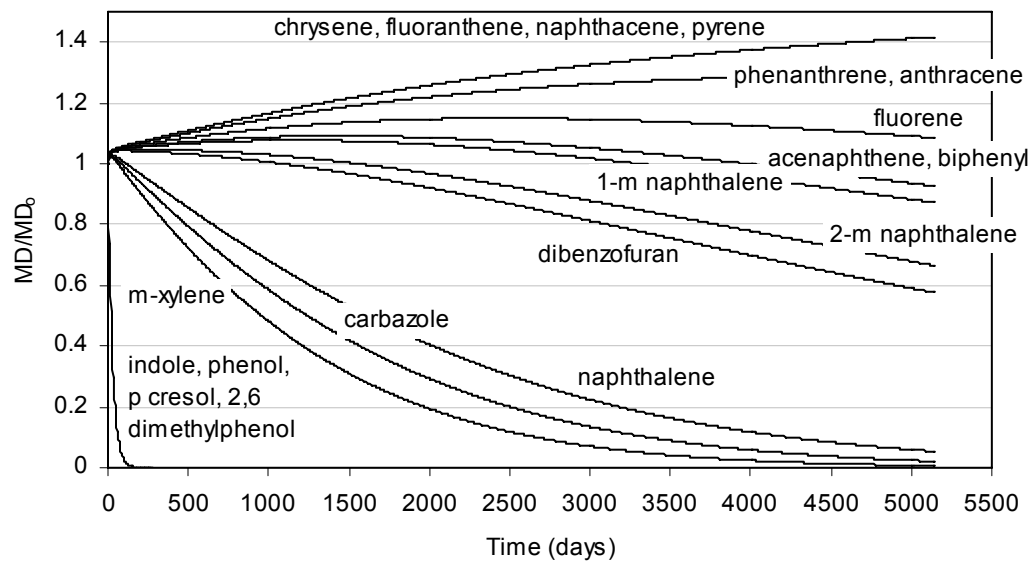


Figure 2.1. Raoult's Law model of creosote source dissolution illustrating the changing relative mass discharge ratios ( $MD/MD_0$ ) of selected compounds over time in groundwater leaving the NAPL.

## 2.4 Methods

Plume development for each organic compound is presented qualitatively using four formats. Contour plots of the maximum concentration detected at each multilevel sampler for a compound are shown in Figure 2.2 (Surfer 8.04, Golden Software Inc). Data from days 626, 1357, 3619 and 5140 since source emplacement illustrate the evolution of the plume.

Total plume mass versus time is also shown in Figure 2.3. The total plume mass was calculated as the sum of the dissolved and sorbed mass. Dissolved mass of a compound was calculated for each sampling event using a three-dimensional integration of the contaminant concentrations. The sorbed mass was calculated using the partitioning coefficient,  $K_d$ , for the compound and assuming sorption ideality. The solids partitioning coefficient was measured or estimated from batch sorption experiments by King et al. (1999). Figure 2.3 displays the results for three compounds, representative of all eleven compounds (refer to Appendix B for the results of other compounds).

By assuming ideal sorption there are several issues which may significantly impact the calculated value of total plume mass for each compound. These potential biases result from physical and chemical non-equilibrium processes. Physical non-equilibrium processes involve the slow mass transport to and from sorption sites which would have the effect of increasing the retardation factor ( $R$ ) of the compound over time resulting in a greater amount of sorbed mass than currently estimated (Ptacek & Gillham, 1992). Chemical non-equilibrium processes include slow adsorption-desorption processes at sorbant surfaces and co-solubility effects of the compounds (Ptacek & Gillham, 1992; Rivett & Allen-King, 2003). The first would serve to increase  $R$  and the amount of mass sorbed whereas the latter, co-solubility effects, would serve to decrease  $R$  in comparison to the equilibrium model of sorption. It is likely that any co-solubility effects would have effected mainly early time (up to day 439 perhaps) when the more soluble, potential cosolvents (phenol and xylenes) were present at their highest concentrations. Issues of non-equilibrium sorption will be explored throughout the



discussions to follow in order to understand what impact higher-than-calculated mass sorption onto solids may have on related calculations and conclusions.

The dissolved mass of individual compounds in the plume was broken down into 32 slices perpendicular to groundwater flow at increasing distance from the source. These approximately 1 m slices each had a mass value which was then plotted versus distance from the source (Figure 2.4). The resulting curves provide an indication of the longitudinal distribution of the plume mass. Again, three compounds, representing the different trends in plume development, are displayed (refer to Appendix B for the results of other compounds).

The detailed monitoring fence at 2.7 m downgradient of the emplaced source is taken as the transition from source zone to plume. The mass discharge of a compound entering the plume (or leached from the source, ML) was calculated at this fence, which has fifteen, 14-point multilevel wells generally spaced at 0.5 m intervals. The fence was divided into individual polygons centered on each sampling point with the boundaries extending halfway to the next sampling point. The discharge was calculated for each polygon as the area times the concentration for the sampling point and the average groundwater flux (0.3 m/day). The sum of the fluxes for these polygons is the resulting mass discharge of the compound leaving the source and entering the plume. The changing mass discharge over time as calculated at the 2.7 m fence and predicted by Raoult's Law is shown in Figure 2.5 for three representative compounds (refer to Appendix B for the results of other compounds).

The mass leached (ML) is taken as the linear interpolation of mass discharge rates at the 2.7 m downgradient fence between synoptic sampling events. When gradual changes in discharge are observed a linear interpolation of mass discharge may be acceptable. Table 2.2 displays negative rates of mass transformation and this likely

reflects uncertainties in mass estimates and the linear interpolation between discharge measurements.

The mass unaccounted for is discussed in Section 2.6 for each compound. The mass unaccounted for (MT) between two sampling dates was taken as the mass leached (ML) minus the change in total plume mass ( $M_T$ ) between the two synoptic sampling days.

$$MT = ML - \Delta M_T \quad (2.3)$$

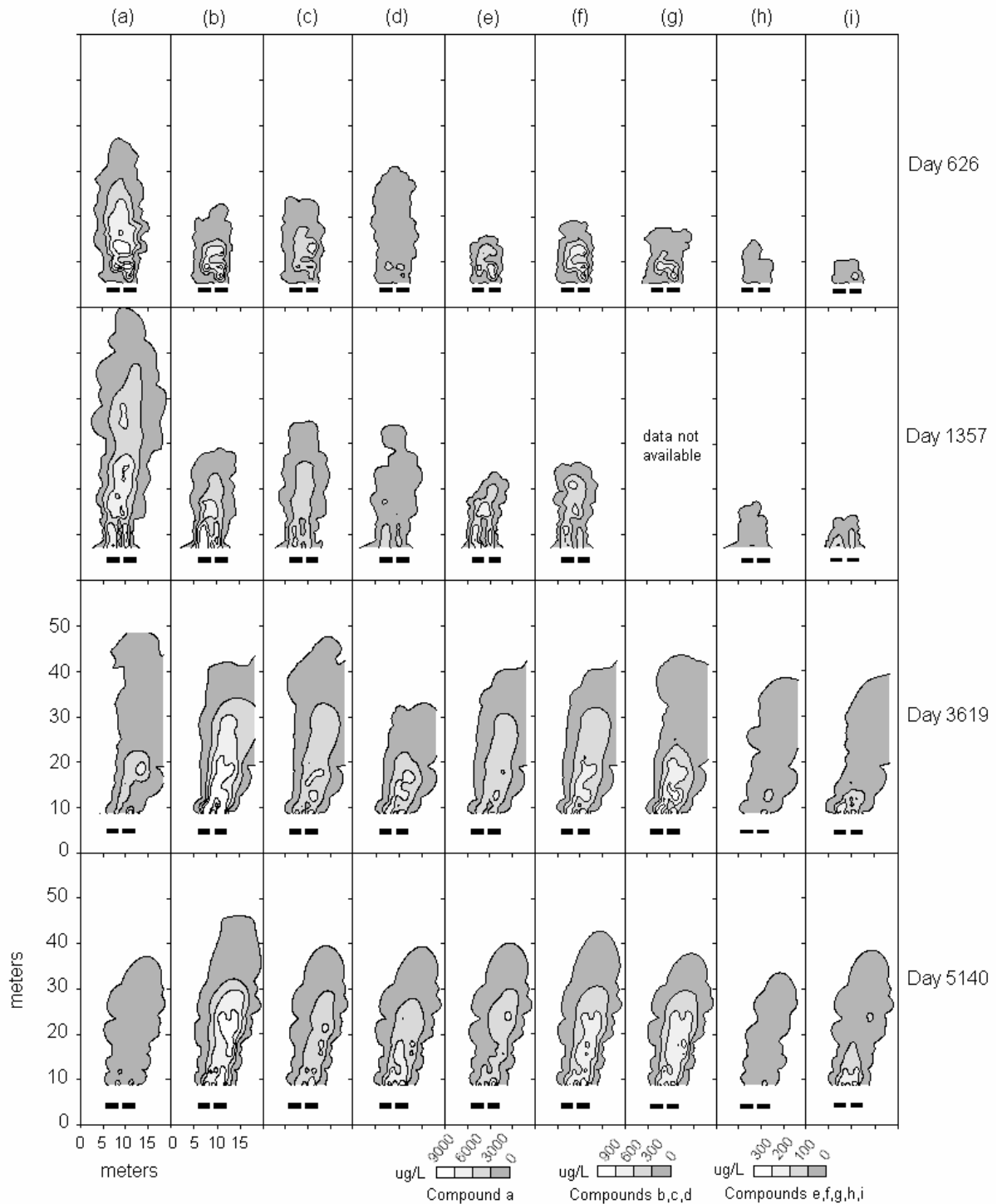


Figure 2.2. Contour plots of (a) naphthalene, (b) acenaphthene, (c) 1-methyl naphthalene, (d) dibenzofuran, (e) carbazole, (f) biphenyl, (g) fluorine, (h) anthracene, (i) phenanthrene at four different times since source emplacement. Contours are based on the maximum concentration detected at each multilevel. The source zone is approximated by the two black rectangles.

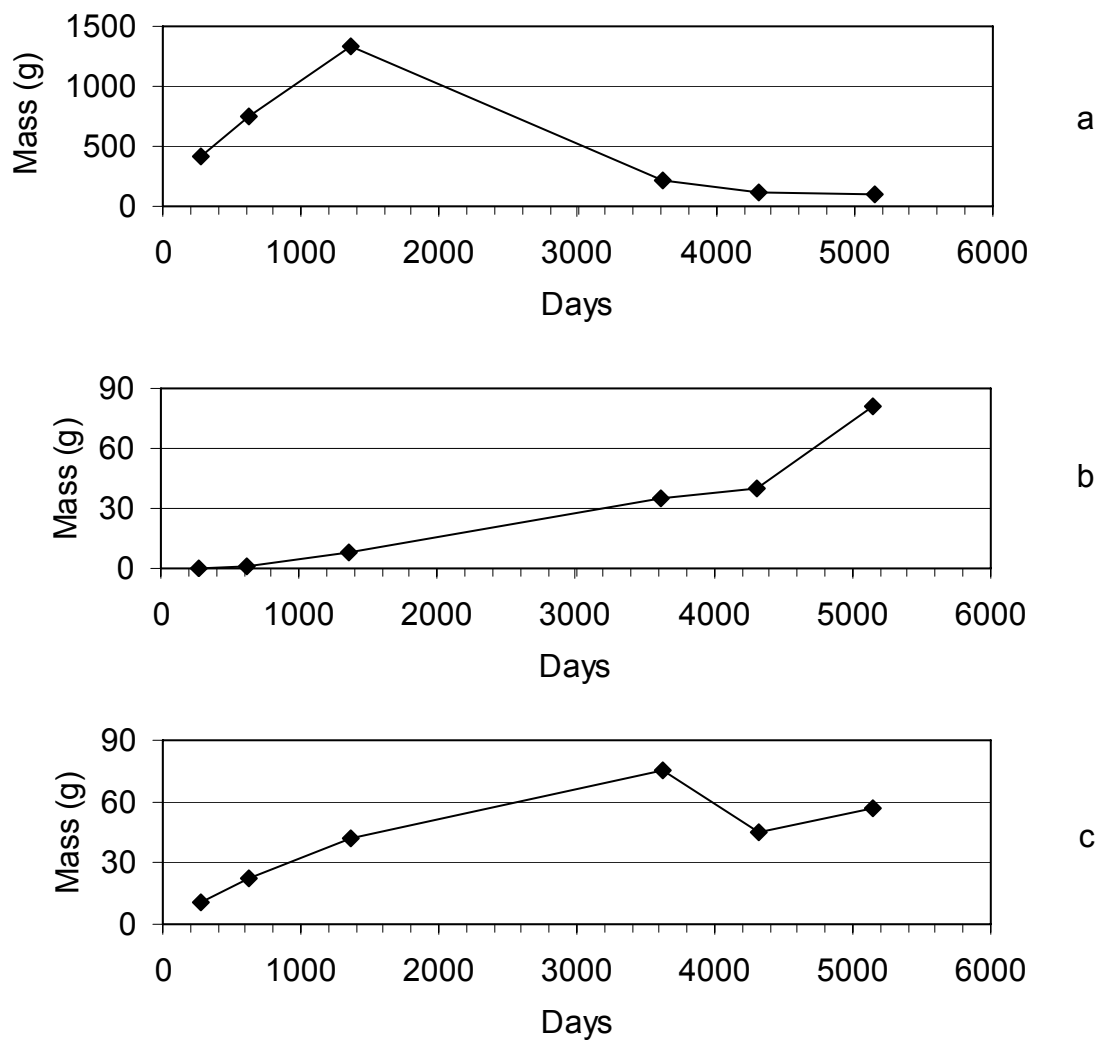


Figure 2.3. Total plume mass (dissolved and sorbed) calculated for (a) naphthalene, (b) phenanthrene and (c) 1-methyl naphthalene versus time since source emplacement.

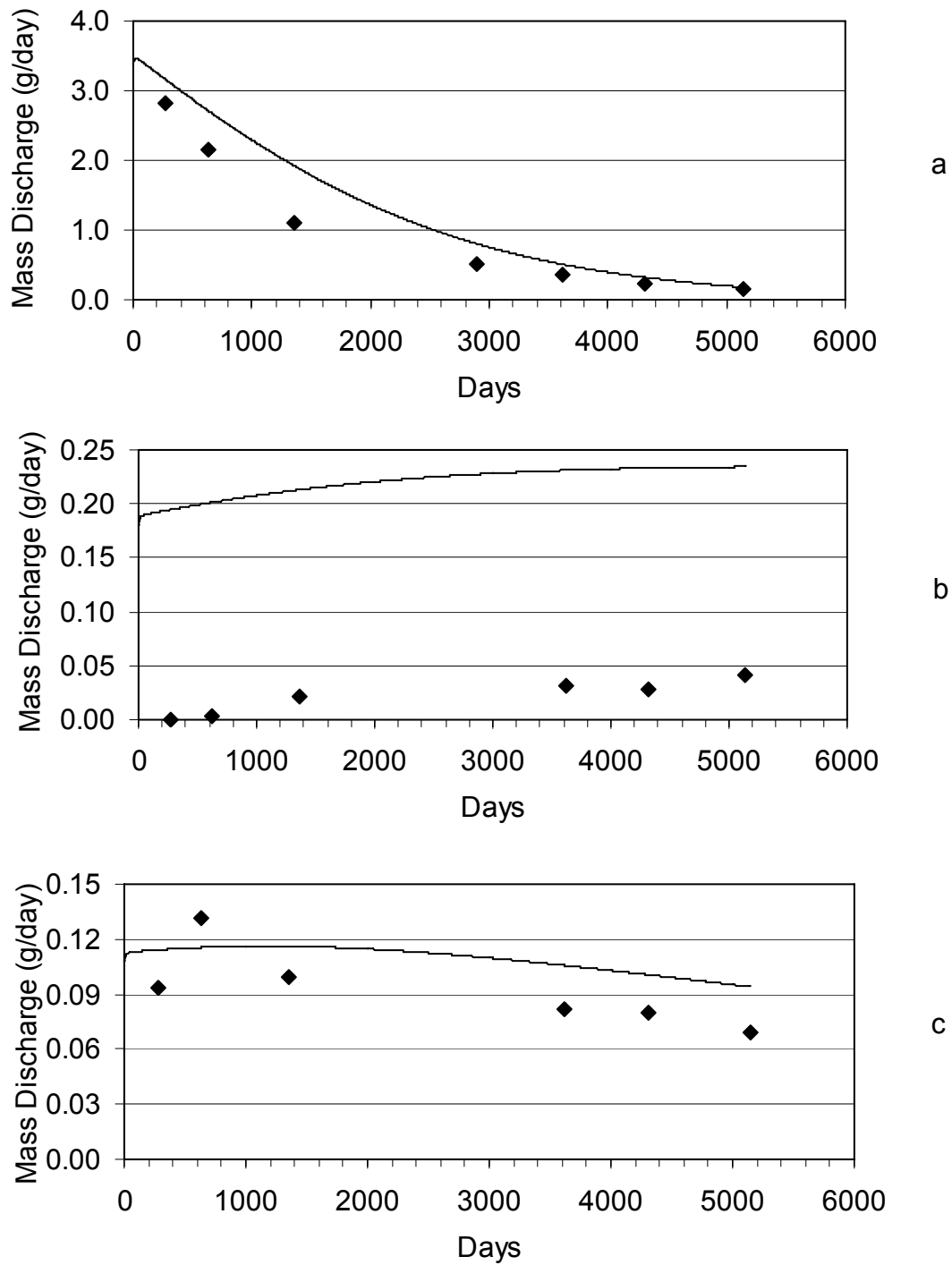


Figure 2.4. Mass discharge of (a) naphthalene, (b) phenanthrene and (c) 1-methyl naphthalene into the plume versus time since source emplacement. Predicted according to Raoult's Law (solid line) and calculated mass flux measured at detailed monitoring fence 2.7 m downgradient of source (points).

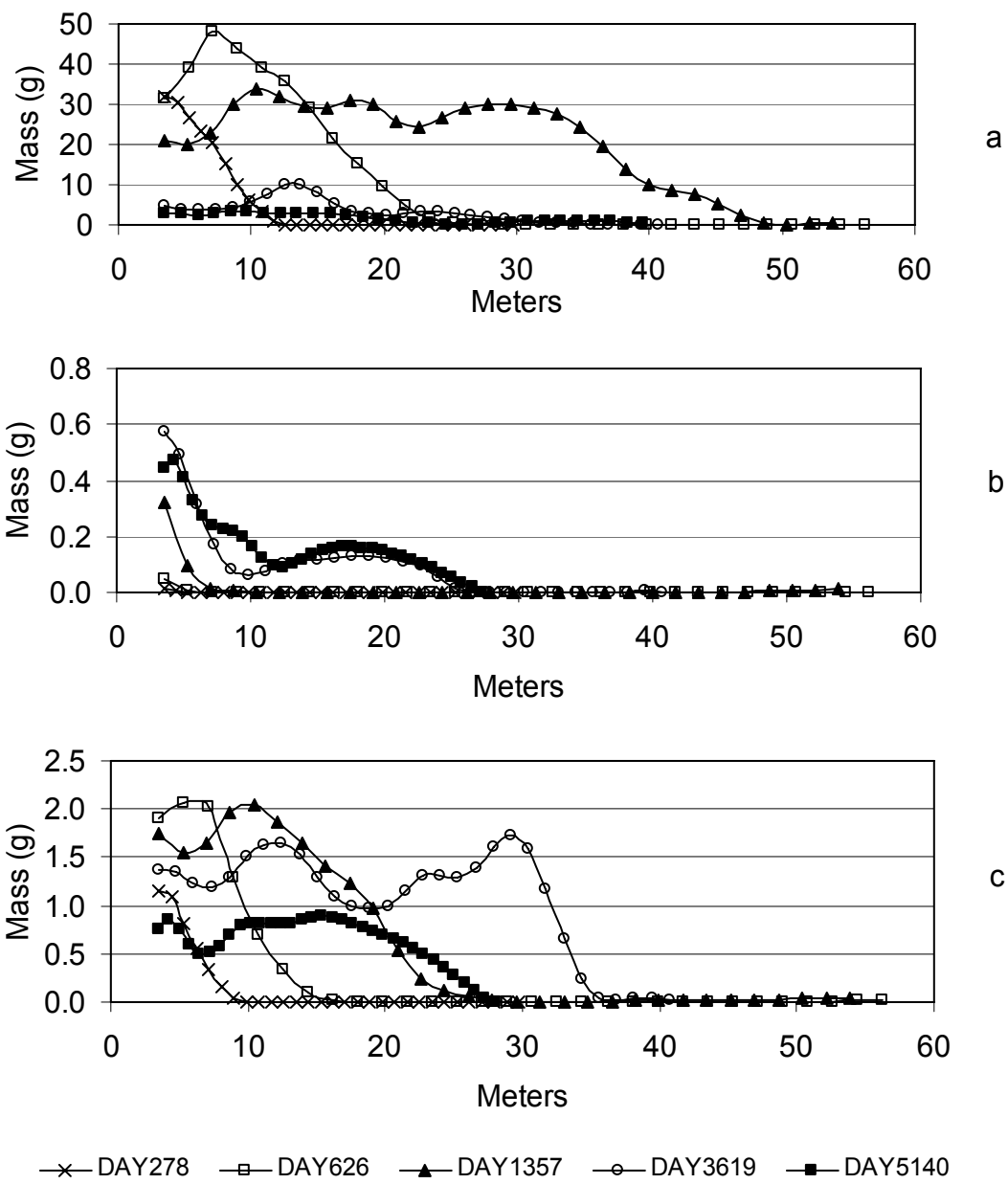


Figure 2.5. Longitudinal distribution of dissolved mass. Dissolved mass of (a) naphthalene, (b) phenanthrene and (c) 1-methyl naphthalene plotted against increasing distance from the source for five different sampling events.

## 2.4.1 Uncertainty

### 2.4.1.1 Mass Discharge

An accurate value of mass discharge is found when the entire contaminant plume is captured by the monitoring network. This is to say an infinite number of sampling points and groundwater fluxes are available for a monitored control plane. The uncertainty in multilevel well mass discharge estimates has been examined by Kubert and Finkel (2006). Based on their assessment, the application of an average groundwater flux to concentrations at the control plane is likely to be among the best approaches. Groundwater flux was calculated using porosity and average linear groundwater velocity ( $q = nv$ ). King & Barker (1999, Table 1) note that the range of groundwater velocity,  $v$ , in this segment of the Borden aquifer is 0.081 to 0.093 m/day and that  $n = 0.33$ . Taking the range of velocity as representing 1 standard deviation (1 SD) and the porosity as exact, the relative uncertainty in estimating  $q$  is then about 10%.

The uncertainty in the average chemical concentration at the fence depends on the analytical uncertainty and likely increases as the density of monitoring points decreases. Laboratory quality assurance reports show variable relative standard deviations for different compounds and different concentrations. However, in general, for the higher concentrations which account for the bulk of the mass flux, the analytical uncertainty (1 SD) is less than about 6%. Béland-Pelletier et al. (in submission) examined the effect of sampling point density on mass discharge estimates using data from the monitoring fence 2.7 m downgradient of the source. On sampling days 3619, 4315 and 5140 this monitoring fence consists of 15 multilevels spaced approximately 0.5 m apart with 14 vertical sampling points, 20 cm apart. This spacing is similar to the geostatistical bed size of  $0.11 \pm 0.02$  m vertical and  $0.91 \pm 1.12$  m horizontal inferred from the semivariograms of  $\ln k$  data by Rivett et al. (2006). Therefore, this sampling density of 6.6 points/m<sup>2</sup> was assumed by Béland-Pelletier et al. to adequately capture the spatial variability of the contaminant distribution across the monitoring fence. Prior to sampling day 3619 the monitoring fence used for mass discharge estimates consisted of 7 wells with 1 m spacing resulting in a sampling density of 4.34 points/m<sup>2</sup>. The analysis by Béland-Pelletier et al. suggests such a sampling density could have a relative uncertainty

of up to 25% (1 SD). On sample day 278 only a selection of wells was sampled resulting in a sample density of 3.6 points/m<sup>2</sup>, similarly with an assigned relative uncertainty of 25% (1 SD). Therefore mass discharge estimates on sampling days 278, 626 and 1357 are considered to have a maximum 1 standard deviation relative uncertainty of 25%.

We assume further that the total relative uncertainty is the square root of the sum of the squared component relative uncertainties (see Béland-Pelletier et al. for discussion). Combining uncertainties in groundwater flux, chemical analyses and monitoring density, suggests the relative uncertainty (1 SD) for mass discharge on days 278, 626 and 1357 should not exceed 28 %, while the uncertainty should approach 12 % for the other snapshots.

#### **2.4.1.2 Plume Mass**

Efforts were made to minimize bias and uncertainty in the total plume mass estimates in this study. With each sampling event the plume was captured in its entirety as shown by non-detect concentrations in wells located downgradient and to the sides of the plume. Sampling density was as high as practical with up to 1 400 samples collected when the naphthalene plume was at its greatest extent (55 m). However, uncertainty in dissolved mass and total mass (dissolved + sorbed) in the plume downgradient of the 2.7 m fence remains.

To estimate the relative uncertainty in dissolved plume mass, findings from two previous natural gradient experiments conducted within the same, densely-monitored segment of the Borden aquifer were reviewed. Hubbard (1992) had conducted a natural gradient injection experiment to explore the long term fate and impact of two gasoline additives. As part of that study three chloride plumes were injected and sampled to their full extent on four different occasions over 376 days. The total mass of chloride (dissolved) estimated with each sampling event ranged within 1.6 to 14% of the total mass injected. Another natural gradient experiment on solute transport conducted within the same monitoring network in the late 1980's revealed total mass estimates ranging from 52% to 116% of the chloride and bromide mass that was actually injected (Mackay et al., 1986; Freyberg, 1986). The low estimates were associated with a low number of sampling points, the lack of sampler density near the center of the plume and incomplete



capture of the plume, none of which occurred in the current experiment. It is perceived that this study most closely resembles that of Hubbard (1992) in regards to sampling density and complete capture of the plume. Therefore, the relative uncertainty in the estimate of total dissolved mass due to monitoring limitations is considered to be no more than 20% (1 SD). Assuming again that the total uncertainty is the square root of the sum of the squared component uncertainties, then the combined analytical uncertainty of 6% with the monitoring uncertainty of 20% was used to estimate the overall relative uncertainty in each dissolved mass as 21% (1 SD). Uncertainty in sorbed mass is even more difficult to quantify, especially given that either experimental or correlation equations were employed. However, a relative uncertainty in estimation of sorbed mass (assuming equilibrium sorption) of no more than 30% was chosen to encompass this ambiguity. Combined with the uncertainty in dissolved mass of 20%, the uncertainty in each estimate of sorbed mass in the plume is considered to be approximately 36%. The relative uncertainty in the total mass in the plume (dissolved + sorbed) will range from 21% (phenol essentially totally dissolved) to 36% for highly sorbed organics. Interpretations need to be consistent with these estimates of uncertainty.

## 2.5 Plume Evolution

Qualitatively, the Raoult's Law model (Figure 2.1) reasonably predicted how the relative mass discharge of nine of the eleven selected compounds changed over time in groundwater leaving the NAPL source zone (Figure 2.4). The exceptions are dibenzofuran and anthracene. The mass discharge of dibenzofuran was expected to decrease over time after a brief initial increase; however, measured discharge continued to increase. Anthracene mass discharge was predicted to increase and then remain relatively constant. The measured discharge decreased after day 3619 (Table 2.2 and Appendix B Appendix B).

For all compounds Raoult's Law predicted mass discharge is greater than that measured at the monitoring fence 2.7 m downgradient of the source. This implies that significant biotransformation was occurring in the source zone. This is supported by dissolved oxygen readings of 3 mg/L upgradient of the source but <1 mg/L at this fence, indicating that oxygen utilization was occurring before this fence.

The temporal behaviour of the eleven compounds falls into three general patterns. Group A shows significant if not complete attenuation by day 1357 or earlier and includes naphthalene, m-xylene and phenol. The mass flux of naphthalene into the plume declined since day 276 (Figure 2.4a); plume mass declined since day 1357 (Figure 2.3a). Phenol was removed from the source within 278 days and m-xylene by day 1357. Phenol was last detected in the plume on day 626 and m-xylene on day 3619. The phenol and m-xylene plumes were described in detail in the previous paper by King et al. (1999) and will not be discussed here.

Another pattern, shown by phenanthrene and dibenzofuran (Group B), is increasing mass flux from the source (Figure 2.4b) and increasing plume mass (Figure 2.3b) over the 5140 days of the study. The plumes increased in extent up to sampling day 3619 and have since remained steady or extended slightly (Figure 2.5b).

Group C consists of 1-methyl naphthalene, carbazole, biphenyl, fluorine, anthracene and acenaphthene. These compounds display a slight increase and then slight decrease in the mass flux leaving the source and entering the plume (Figure 2.4c), but generally increasing total plume mass until at least day 3619 (Figure 2.3c). Exceptions

are fluorine and biphenyl which have shown a consistent and increasing plume mass since day 3619. The maximum extent of the dissolved plumes was reached on day 3619 and then there was minor shortening for anthracene and minor extension for acenaphthene (Figure 2.2).

## 2.6 Mass Unaccounted For

Natural attenuation is an important process limiting plume development. The expected plume lengths after 5140 days for ten compounds was calculated assuming only advection and retardation processes were occurring (see Table 2.1). Retardation values (R) were calculated using sorption coefficients ( $K_d$ ) determined through laboratory batch testing by King et al. (1999), with porosity of 0.33 and a bulk density of  $1.81 \text{ g/cm}^3$  assumed to obtain R. Anthracene, acenaphthene, biphenyl, fluorene and xylene were not considered in the batch tests and so literature values of  $\log K_{ow}$  were used with the following empirical relationship (Karickhoff et al., 1979) and a  $f_{oc}$  value of 0.0002 (King & Barker, 1999) to calculate a value for  $K_d$ .

$$\log K_{oc} = 1.00 \log K_{ow} - 0.21 \quad (2.4)$$

$$K_d = f_{oc} K_{oc} \quad (2.5)$$

Table 2.1. Actual plume lengths based on concentrations detected furthest from the source on day 5140 and predicted plume lengths of compounds based on  $K_d$  values. Xylene reached its greatest extent on day 626 at approximately 30 m and was last detected on day 3619.

Chemical	$K_d^a$	R <sup>c</sup>	Extent of Plume (m)	
			Predicted	Actual
xylene	0.11 <sup>b</sup>	2.2	210	-
naphthalene	0.22	2.2	210	41
1-m naphthalene	0.24	2.3	200	41
acenaphthene	0.51 <sup>b</sup>	6.6	70	26
biphenyl	0.58 <sup>b</sup>	7.5	62	26
dibenzofuran	0.67	4.7	99	22
carbazole	0.83	5.6	83	22
fluorene	0.93 <sup>b</sup>	11.2	41	22
anthracene	1.73 <sup>b</sup>	20.1	23	22
phenanthrene	1.80	10.9	43	22

<sup>a</sup>determined from laboratory batch testing by King et al (1999)

<sup>b</sup>from literature values of  $\log K_{ow}$  using  $\log K_{oc} = 1.00 \log K_{ow} - 0.21$  and  $K_d = f_{oc} K_{oc}$

<sup>c</sup>Associated estimates of R according to  $R = 1 + (\rho/\eta)K_d$

The results show that after 5140 days the actual plume length for all the compounds is less than the predicted length based on advection and simple retardation alone. This illustrates that mass transformation may be playing a key role in limiting plume extent. The difference between the actual and predicted plume lengths is far less for the more retarded compounds. This may reflect bias' imparted from the simple adsorption model that had been applied to determine the predicted plume lengths rather than biotransformation processes. Studies have shown that R is dependent on groundwater velocity, time and the traveled distance (Roberts et al., 1986; Ptacek & Gillham, 1992). Ptacek & Gillham (1992) conducted field- and lab-column experiments to estimate retardation coefficients of five halogenated hydrocarbons in the Borden aquifer. They found that R increased as the average pore-water velocity in the columns decreased and that there were large deviations in R for longer travel times. They found batch experiments conducted over a short time period (24 hours) represent earliest uptake of the organic compounds by the aquifer material. Sorption experiments conducted over a longer time period (months) indicated a small amount of uptake continued to occur long after an initial period of rapid uptake. Ptacek & Gillham ascertain the slow sorptive process may account for the large deviation between the laboratory batch results and long-term field behaviour. Overall they found calculated values of R to be generally lower than the measured values.

Roberts et al. (1986) observed compounds to migrate at an average velocity that was less than that of a conservative tracer and the migration was observed to decrease over time. The decrease in migration rate was attributed to a non-equilibrium transport process due to delayed access to sorptive sites by diffusion into aquifer grains. The decrease in the rates of migration of all reactive solutes was greatest during the first several months after injection and the greatest decrease in migration rates was observed for the least soluble and least mobile compounds (Roberts et al., 1986).

In this thesis, synoptic mass measurements were used to estimate the extent of mass unaccounted for. Assuming all the mass unaccounted for was biodegraded the rates of mass transformation were calculated. The results are shown in Table 2.2. The rate of input of m-xylene into the plume declined as predicted (Figure 2.1) and high initial mass transformation rates in the plume (0.9 – 3 g/day) resulted in the majority of m-xylene

being removed by day 3619. Naphthalene had the highest mass leached from the source into the plume as well as the most mass apparently transformed and it formed the dominant plume up to day 1357 (King & Barker, 1999). The rate of mass discharge of naphthalene into the plume was higher and continued longer, reflecting the larger mole fraction and lower solubility of naphthalene in the source. The greater input rate of naphthalene and similar mass transformation rates resulted in the mass of naphthalene in the plume reaching its maximum on day 1357 (Figure 2.3a), while the m-xylene plume mass peaked on day 278. Even though naphthalene input into the plume continually declined (Figure 2.4a), the declining mass transformation rate (Table 2.2) resulted in significant naphthalene remaining to the end of the monitoring period. The electron acceptor (EA) utilization by biotransformation of less-retarded and readily degradable phenols and xylenes at early time likely allowed the naphthalene plume to grow in the EA-reduced “shadow” even when the flux from the source was declining. Figure 2.5a shows the very significant decline of dissolved naphthalene mass throughout the plume after day 1357. The near-source mass may have begun declining before day 1357 (Figure 2.5), consistent with the declining naphthalene input rate. By day 3619 the naphthalene mass being transformed was greater than the mass entering the plume indicating that biodegradation exceeded leaching from the source. This is expected to continue and so the naphthalene plume should continue to shrink.

In contrast to Group A chemicals, the plumes of Group B, phenanthrene and dibenzofuran, show a much lower flux out of the source and a much reduced rate of mass transformation. Dibenzofuran mass input was greater and exceeded mass transformation initially and so it formed the more extensive plume. Phenanthrene mass input rate increased to exceed its mass transformation rate and so its extent increased to about that of dibenzofuran by day 3619. Figure 2.5c shows increased input, downgradient extent and mass increase generally throughout the plume. Group B chemicals are expected to continue to increase in size with time as input into the plume still exceeds apparent transformation.

Table 2.2. Tabulated mass balance results for 1. m-xylene, 2. naphthalene, 3. phenanthrene, 4. dibenzofuran, 5. carbazole, 6. 1-methyl naphthalene, 7. anthracene, 8. acenaphthene, 9. biphenyl and 10. fluorine.

Compound	1 mxyz	2 naph	3 phen	4 diben	5 carb	6 1-mnaph	7 anth	8 acenap	9 biphen	10 fluor
<b>Initial Source Mass (g)</b>	2850	7110	9150	3240	242	1420	913	5260	1100	3760
<b>Plume Mass (g)</b>										
<b>Dissolved (M<sub>D</sub>)<sup>a</sup></b>										
	278	340	190	0.030	2.9	0.80	4.8	0.080	5.7	1.0
	626	140	340	0.10	5.9	2.0	9.5	0.38	10	3.7
	1357	54	600	0.73	5.0	3.2	18	0.55	20	3.9
	3619	2.6	99	3.2	19	8.6	32	2.2	51	11
	4315	0.50	49	3.7	16	3.9	19	2.2	40	8.4
	5140	0	48	7.5	38	7.3	24	1.4	56	14
<b>Sorbed (M<sub>S</sub>=M<sub>D</sub>(R-1))</b>										
	278	230	220	0.28	11	3.7	6.3	0.42	13	2.5
	626	93	410	1.0	22	9.0	13	2.0	22	9.1
	1357	37	730	7.3	19	15	24	3.0	45	10
	3619	1.8	120	31	69	39	43	12	110	26
	4315	0.35	60	36	58	18	25	12	91	21
	5140	0	58	74	140	33	32	7	130	36
<b>Total (M<sub>T</sub>=M<sub>D</sub>+M<sub>S</sub>)</b>										
	278	580	410	0.31	14	4.5	11	0.5	18	3.5
	626	230	750	1.1	28	11	22	2.4	31	13
	1357	92	1300	8.0	24	18	42	3.5	64	14
	3619	4.4	220	35	88	48	75	14	170	37
	4315	0.9	110	40	73	21	45	14	130	29
	5140	0	110	81	180	41	57	8.8	180	50
<b>Mass Input (g/day)<sup>b</sup></b>										
	278	3.0	2.8	0.0007	0.066	0.024	0.093	0.0020	0.13	0.025
	626	1.0	2.2	0.0030	0.079	0.043	0.13	0.0090	0.22	0.063
	1357	0.28	1.1	0.021	0.078	0.016	0.10	0.010	0.19	0.017
	3619	0.0040	0.34	0.031	0.10	0.022	0.082	0.011	0.17	0.034
	4315	0.013	0.24	0.028	0.11	0.014	0.080	0.0080	0.14	0.039
	5140	0	0.16	0.041	0.12	0.025	0.068	0.0070	0.14	0.038
<b>Mass Leached, ML (g)<sup>c</sup></b>										
0-278	830	780	0.19	18	6.7	26	0.56	37	7.0	5.1
278-626	700	870	0.64	25	12	39	1.9	61	15	13
626-1357	470	1200	8.8	57	22	84	6.9	150	29	152
1357-3619	320	1600	59	200	43	210	24	400	57	152
3619-4315	6.0	200	21	71	13	56	6.6	110	25	26
4315-5140	5.5	160	28	94	16	61	6.2	120	32	29
<b>Mass Unaccounted For, MT (g)</b>										
0-278	260	370	-0.12	4.8	2.2	15	0.056	18	3.5	2.8
278-626	1000	530	-0.11	11	5.1	28	-0.0060	48	6.1	8.7
626-1357	610	600	1.9	62	15	64	5.8	120	28	119
1357-3619	410	2700	32	132	13	172	13	300	33	119
3619-4315	10	310	15	86	39	87	6.4	140	33	35
4315-5140	6.3	170	-13	-8.8	-3.2	49	11	65	11	2.2
<b>Mass Transformation Rates (g/day)<sup>d</sup></b>										
0-278	0.93	1.3	0	0.017	0.0080	0.053	0	0.066	0.012	0.010
278-626	3.0	1.5	0	0.032	0.015	0.081	0	0.14	0.018	0.025
626-1357	0.83	0.82	0.0025	0.084	0.020	0.087	0.0080	0.16	0.039	0.040
1357-3619	0.18	1.2	0.014	0.058	0.0057	0.076	0.0059	0.13	0.015	0.050
3619-4315	0.014	0.45	0.022	0.12	0.056	0.12	0.0093	0.20	0.047	0.050
4315-5140	0.0077	0.20	-0.016	-0.01	-0.004	0.060	0.014	0.078	0.013	0.0026

<sup>a</sup>Calculated from synoptic monitoring data

<sup>b</sup>Calculated with synoptic monitoring data from a fence 2.7 meters downgradient of the source. See section 5 for details

<sup>c</sup>Linear interpolation of mass flux between synoptic monitoring events

<sup>d</sup>Assuming all mass unaccounted for was biodegraded

Mass input rates for Group C chemicals are generally low ( $< 0.2$  g/day) without major temporal trends while mass transformation rates are generally low, consistent with these plumes extending further downgradient at least to day 3619. 1-methyl naphthalene shows dissolved mass extending downgradient reasonably regularly until day 3619 and then shows a significant loss of mass from the front of the plume (Figure 2.5b). For Group C chemicals, carbazole, 1-methyl naphthalene, anthracene, acenaphthene, biphenyl and fluorene, the mass transformation rates are similar to their mass input rates so these plumes may be reaching their maximum extent.

The impact that the assumption of ideal sorption has on the mass transformation rates must be considered. Given the possibility that the amount of mass sorbed is underestimated, the mass transformation rates could very well be less than presented in Table 2.1. This would mean the amount of mass unaccounted for is composed of a fraction of mass that has been biotransformed and a remaining mass that is sorbed within the aquifer which would result in lower calculated rates of mass transformation. Roberts et al. (1986) quantified estimates of R for four compounds, carbon tetrachloride ( $R = 1.6-2.5$ ), bromoform ( $R = 1.5-2.8$ ), tetrachloroethylene ( $R = 2.7-5.9$ ) and dichlorobenzene ( $R = 1.8-9.0$ ) for a 2 year period. Hexachloroethane values of R were also reported for early time ( $R = 1.2-7.9$  for  $t < 85$  days) but was not reported for late time due to a large disappearance of mass. This study shows that for the more sorbing compound, dichlorobenzene ( $\log K_{ow} = 3.4$ ), the value of R increased five fold over the 2 year study.

The rate of increase in R was initially rapid but retardation appeared to still be increasing, at a slower rate, at the end of the almost 2 year study by Roberts et al. (1986). Considering the compounds followed in the present study all have greater  $\log K_{ow}$  values and considering the 14-year length of the current study, it is possible that the associated values of R have increased substantially beyond the short-term equilibrium values of King et al. (1991) employed in calculations in this thesis. This would drastically increase the amount of sorbed mass within the plume and as a result significantly decrease the calculated mass transformed and the rate of mass transformation, at least of the more highly sorbed compounds. It is difficult to quantify this effect, but Table 2.3 illustrates the recalculated values for late time, day 5140, assuming R values five times those reported by King et al. (1991).



Table 2.3. Tabulated mass balance results for late time assuming a retardation value 5x that used in Table 2.2 for 1. m-xylene, 2. naphthalene, 3. phenanthrene, 4. dibenzofuran, 5. carbazole, 6. 1-methyl naphthalene, 7. anthracene, 8. acenaphthene, 9. biphenyl and 10. fluorine.

Compound	1	2	3	4	5	6	7	8	9	10	
	mstyl	naph	phen	diben	carb	1-mnaph	anth	acenap	biphen	fluor	
<b>Initial Source Mass (g)</b>	2850	7110	9150	3240	242	1420	913	5260	1100	3760	
<b>Plume Mass (g)</b>											
<b>Dissolved (<math>M_D</math>)<sup>a</sup></b>											
	4315	0.50	49	3.7	16	3.9	19	2.2	40	8.4	7.0
	5140	0	48	7.5	38	7.3	24	1.4	56	14	13
<b>Sorbed (<math>M_S=M_D(R-1)</math>) where <math>R = 5R</math></b>											
	4315	3.8	490	200	350	100	200	68	610	140	150
	5140	0	480	400	850	200	260	43	850	240	280
<b>Total (<math>M_T=M_D+M_S</math>)</b>											
	4315	4.3	540	200	370	110	220	70	650	150	160
	5140	0	530	400	880	200	280	44	910	250	290
<b>Mass Input (g/day)<sup>b</sup></b>											
	4315	0.013	0.24	0.028	0.11	0.014	0.080	0.0080	0.14	0.039	0.033
	5140	0	0.16	0.041	0.12	0.025	0.068	0.0070	0.14	0.038	0.039
<b>Mass Leached, ML (g)<sup>c</sup></b>											
	4315-5140	5.5	160	28	94	16	61	6.2	120	32	29
<b>Mass Unaccounted For, MT (g)</b>											
	4315-5140	9.8	170	-180	-420	-80	1.6	32	-140	-73	-110
<b>Mass Transformation Rates (g/day)<sup>d</sup></b>											
	4315-5140	0.012	0.21	-0.22	-0.51	-0.10	0.0020	0.039	-0.17	-0.089	-0.13

<sup>a</sup>Calculated from synoptic monitoring data

<sup>b</sup>Calculated with synoptic monitoring data from a fence 2.7 meters downgradient of the source. See section 5 for details

<sup>c</sup>Linear interpolation of mass flux between synoptic monitoring events

<sup>d</sup>Assuming all mass unaccounted for was biodegraded

Assuming a retardation value of five fold clearly results in the amount of mass in the plume to exceed the amount of mass that has entered the plume for six of the ten compounds studied for the last monitoring period as indicated by the negative values of mass unaccounted for in Table 2.3. This over estimation of the mass unaccounted for is obviously not physically possible indicating that a five fold increase in retardation values is likely not a realistic issue. The same calculations performed with a two fold increase in retardation values produces similar results to Table 2.2. However, instead of three compounds essentially having ~0 g of mass unaccounted for a two fold retardation value causes two compounds, dibenzofuran and biphenyl, to have essentially 0 g of mass unaccounted for and two compounds, phenanthrene and carbazole, clearly showing more mass within the plume than that which has entered the plume. Therefore the retardation

values may be greater than that initially calculated due to non-equilibrium sorption however it is unlikely that they are as great as five times that predicted.

## 2.7 Biotransformation Controls

Previous studies demonstrated that indigenous aquifer microorganisms could degrade creosote compounds aerobically. King et al. (1999) conducted aerobic microcosm experiments with and without the addition of nutrients. They observed that biodegradation of phenol, naphthalene, dibenzofuran, carbazole and 1-methyl naphthalene occurred without the addition of nutrients. The rate of biodegradation was greatest for naphthalene and carbazole. When nutrients were added biodegradation was more rapid. Both m-xylene and phenanthrene were recalcitrant without the addition of nutrients, but with nutrient addition m-xylene was completely degraded within the 135 day experiment and phenanthrene had shown about 75% biotransformation.

Interactions among degrading coal tar creosote compounds are anticipated (Arvin & Flyvbjerg, 1992; Millette et al., 1998; Zamfirescu & Grathwohl, 2001). In a column study, Millette et al. (1998) observed that the presence of phenanthrene inhibited fluorene and possibly carbazole biotransformation. It is possible that the presence of chemicals such as phenanthrene within the plume may have reduced the biotransformation of carbazole, especially after day 1357 when these plumes overlap (Figure 2.2). Zamfirescu & Grathwohl (2001) suggested that acenaphthene would only degrade in the presence of naphthalene. Martin (2004) performed an aerobic microcosm study using soil from within the creosote plume and with nutrients added, comparing the aerobic degradation of naphthalene in the presence of 1-methyl naphthalene and acenaphthene and the degradation of these compounds separately. Martin found that all three compounds, when incubated alone, degraded to below detection limits within the 8 day study. The microcosms that contained the mixture of all three compounds showed that both naphthalene and 1-methyl naphthalene biodegradation was not affected by the presence of the other compounds. However, acenaphthene was more easily degraded in the presence of naphthalene and/or its degradation products. This may be reflected in the increase in acenaphthene plume mass between days 4315 and 5140 and a decline in the acenaphthene rate of biotransformation in that period, when the naphthalene plume had only low mass throughout its plume (Figure 2.5c). However, Millette et al. (1998) noted that interactions seen in static batch microcosms and in a hydrodynamic saturated column

study differed and consequently it is not clear that expectations derived from the static microcosm study by Martin et al. (2004) are reliably applicable to the Borden field case.

While substrate interactions may be important in controlling the patterns of biodegradation, all chemicals followed in this experiment seem to degrade readily under at least aerobic conditions. Electron acceptors are likely a major control over the extent of degradation. Electron acceptor distributions were evaluated to determine if the mass loss of creosote compounds could be supported by the utilization of the stoichiometric mass of electron acceptors. Dissolved oxygen is the primary electron acceptor at the site. Background concentrations of dissolved oxygen taken from a monitoring fence approximately 2 m upgradient of the source on day 5140 averaged 3 mg/L. Within the core of the plume concentrations detected are all less than 0.6 mg/L. In front of the detectable creosote compound plumes a depleted dissolved oxygen shadow remains as predicted in the modeling of hydrocarbon plumes by Molson et al. (2002).

Within the organic compound plumes depletion of oxygen was evident, but minimal changes in nitrate, iron (FeII), sulphate and methane (CO<sub>2</sub> utilization) concentrations were seen on day 5140 (Table 2.4). The mass ratio of oxygen and dibenzofuran consumed as per equation 5 is also shown.



Dissolved oxygen is the major electron acceptor at the site, therefore the stoichiometric mass ratios of 10 compounds listed in Table 2.2 were used to determine the amount of oxygen required to account for the mass loss (as estimated according to Raoult's Law model of source dissolution) of the compounds by oxidation alone, assuming complete mineralization. The required oxygen was then compared to the total oxygen available, determined using the average background oxygen concentration for day 5140 (3 mg/L) multiplied by the flux (0.03 m/day) and the cross-sectional area of the contaminant plume (31 m<sup>2</sup>). The cross-sectional area includes an additional cross-sectional area on the periphery of the chemical plume to account for oxygen that could become available via transverse dispersion during downgradient transport.

Table 2.4. Average concentrations within the plume and background for select inorganic parameters. Note that Iron-Total should be essentially equivalent to Fe<sup>2+</sup> at the near neutral pH of the groundwater. Stoichiometric mass ratio of primary electron acceptor to organic compound for dibenzofuran is shown for comparison.

Parameter	Detection Limit mg/L	Background		Within Plume		Dibenzofuran Stoichiometric Mass Ratio (Parameter:Organic)
		Average mg/L	n	Average mg/L	n	
Dissolved Oxygen	<sup>a</sup>	3.0	12	<1	242	2.57
Sulphate	2	20	12	20	229	3.86
Nitrate -NO <sub>3</sub> -N	0.1	0.3	12	0.5	233	3.98
Iron - Total	0.02	0.08	12	0.24	99	17.93
Manganese	0.2	0.54	12	0.96	103	8.82
Methane	0.3 ug/L	7 ug/L	12	9 ug/L	34	0.65

<sup>a</sup>+/- 0.5% of measured value +/-1 digit at 5 to 30 degrees C.

To estimate the increase in cross-sectional area due to transverse dispersion, three approaches were used. The first examines the increase in cross sectional area of the chemical plumes downgradient relative to the emplaced sources. The naphthalene plume widened by 2.2 m and thickened by 0.9 m at about 20 m downgradient of the source. It is anticipated that an even wider plume would have resulted without biodegradation. Next, the distribution of the conservative tracer, Cl, in the Stanford/Waterloo experiment (MacKay et al., 1986) conducted in the same aquifer segment was examined to estimate its increase in cross-sectional area. This Cl plume grew from 9 m wide by 3.2 m thick to about 12 m wide by 3.2 m thick from day 1 to day 462 and after having migrated about 40 m downgradient (Mackay et al., 1986, Fig. 8 and 9). This was also about the maximum longitudinal extent of the naphthalene plume in our study (Figure 2a). Thus, the Cl plume widened 3 m horizontally and negligibly vertically. Lastly, the method of Freeze and Cherry (1979, p. 395) was used to estimate that the zone in which 99.7% of the plume mass would occur would increase about 2.8 m horizontally and 0.28 m vertically during about 40 m (440 days) of advection and dispersion, in good agreement with the observed growth of both the Cl plume and our naphthalene plume. Accordingly transverse dispersion was considered to have potentially widened the chemical plumes by 2.2 m and thickened them by 0.9 m. In addition, oxygen migrating within some area fringing this enlarged cross-section could also have dispersed into the chemical plumes.

By inference from the degree of transverse spreading estimates above, an additional 2.8 m horizontal and 0.28 m vertical is added to the cross-sectional area potentially providing oxygen to support aerobic biodegradation. Thus, the cross-section from which oxygen was potentially available was considered to 31 m<sup>2</sup>.

The flux of oxygen determined to be, 2.79 g/d, was then applied to the 5140 day period to determine the maximum mass of oxygen available during the monitoring period (Table 2.5). For all the time steps inspected the amount of oxygen required to support the apparent loss of organic compounds far exceeded the calculated amount of oxygen available.

The calculations were then repeated assuming only partial mineralization of the compounds to salicylic acid. Previous studies (King et al., 1999) found mg/L concentrations of organic acids including salicylic acid, likely the products of partial mineralization. This comparison of oxygen required for each compound assuming complete mineralization and partial mineralization to salicylic acid is shown in Table 2.5.

Table 2.5. Calculations comparing the amount of organic lost with the calculated amount of oxygen required if that organic was lost solely due to oxidation. The total oxygen required was then compared to the amount of oxygen available to the plume.

Compound	Stoichiometric Mass Ratio		Mass Transformed <sup>a</sup> (g)	Day 0-5140 Required amount of O <sub>2</sub> (g)	
	Complete mineralization	Partial (salicylic acid)		Complete	Partial
	O <sub>2</sub> :organic	O <sub>2</sub> : Organic			
m-xylene	3.17	1.05	2838	8996	2980
naphthalene	3.24	1.24	6745	21854	8364
dibenzofuran	2.57	1.23	1807	4644	2223
phenanthrene	2.96	1.70	1102	3262	1873
carbazole	2.97	1.57	198	588	311
1-m naphthalene	3.04	1.35	529	1608	714
anthracene	2.96	1.70	112	332	190
biphenyl	3.00	1.45	366	1098	531
fluorene	2.98	1.64	957	2852	1569
acenaphthene	3.00	1.45	1802	5406	2613
Total O <sub>2</sub> Required:				50640	21368
Total O <sub>2</sub> Available <sup>b</sup> :				14197	

<sup>a</sup> Based on the amount of mass leached from the source up to day 5140 as predicted by the Raoult's Law Model.

<sup>b</sup> Based on an average background dissolved oxygen concentration of 3 g/m<sup>3</sup>, a darcy flux of 0.03 m/day and a 31 m<sup>2</sup> cross sectional area of oxygen available to the plume through advection and dispersion.

Partial mineralization significantly reduces the stoichiometric mass ratio of oxygen to organic (from an average of 3 to 1.5), but still the oxygen demand cannot be met. In addition the amount of oxygen available for degrading the ten compounds considered is likely overestimated in these calculations, as degradation of other compounds (phenols, xylene, etc.) was not considered.

It was previously determined that values of sorbed mass may be significantly underestimated (Chapter 2.6). If the field-scale, long-term retardation factors for the compounds were five times those employed in calculations in Table 2.2., the sorbed mass in the plume for day 5140 would be about 5 times greater than currently calculated. The resulting increase in sorbed mass on day 5140 would reduce the amount of mass that would appear to have been transformed (mass leached from the source minus the mass in the plume) from ~16 000 g to ~13 000 g of organics. The oxygen requirements to transform this amount of mass would be reduced to ~17 000 g. If the *in situ* chemical oxidation of the source zone is considered, assuming all the permanganate reacted with the creosote compounds, this would account for up to 6 000 g of organic compounds transformed. It is known that not all the permanganate reacted within the source zone (Chapter 3.3) however if even just 30% of permanganate reacted with the creosote compounds this would decrease the amount of oxygen required by 3 000 g. Consideration of non-equilibrium sorption and the effect of the ISCO could bring the amount of oxygen required, well within the oxygen available to the organics by day 5140 assuming partial mineralization. This example demonstrates the sensitivity of the mass transformed calculation to the underlying assumption of ideal sorption.

In the summer of 2006 samples were collected from the core of the plume where King et al. (1999) previously detected around 2 700 µg/L aromatic acids including about 50 µg/L benzoic acid. In the more recent analysis a less-sensitive high performance liquid chromatograph (HPLC) method was used with a detection limit of 2 mg/L benzoic acid. Benzoic acid was not detected and further peaks of aromatic acids in the range of C<sub>5</sub> to C<sub>7</sub> were not seen in the chromatogram. Perhaps the intermediate biotransformation

products seen by King et al. in 1999 had also been biotransformed or had advected further downgradient beyond the monitoring network.

Given the chemical complexity of coal tar creosote plumes and the potential for incomplete mineralization, there was interest in whether biotransformation significantly reduced aquatic toxicity of the plume. Toxicity testing in 1995 (Maude, 1996) found a significantly higher toxicity in the depleted dissolved oxygen shadow in front of the plume where no creosote compounds are detected when compared to background. Maude found that samples collected in front of the plume had an effect on the reproduction of *Ceriodaphnia dubia* with an IC25 value of 28.2%; however the samples did not cause lethality (LC50 value of 100%). The increased toxicity may reflect breakdown products found here as a result of partial mineralization. In 2006, samples were collected to repeat the *C. dubia* assay (Appendix C **Error! Reference source not found.**). In this updated round of sampling, the Environment Canada protocol for the *C. dubia* assay was followed (Environment Canada, 1997) and samples were collected from background, within the dissolved plume and in front of the plume but within the depleted dissolved oxygen shadow. Neither background nor the sample in the depleted oxygen shadow caused lethality or adversely impacted the reproductive success in *C. dubia*. The sample from within the plume did affect the survival and reproduction of *C. dubia* as indicated by the LC50 value of 62.2% and the IC25 value of 26.8%. Thus the mobile toxicity agent(s) indicated in 1995 did not appear to persist into 2006.

Another effort was to assess whether the understanding of biodegradation was sufficient to apply conceptually simple numerical models and at least “match” the major features of the field data. Attempts were made to model the naphthalene plume up to day 3619 (Martin et al., 2005) using visual MODFLOW and RT3D with three electron acceptors. Two approaches to the biotransformation process were used, a simple first order rate law model and a more complicated electron acceptor model. When providing a reasonable match to the naphthalene plume extent, both models over estimated the amount of mass degraded in the core of the plume resulting in a poor match to the high concentration data. Attempts were made to account for removal of naphthalene within the source by creating a zero-electron acceptor zone behind the simulated input into the plume segment. While this simulated the early time naphthalene data, the late time



simulations suffered the same inadequacy. This experience suggests that naphthalene biodegradation is complex, perhaps with temporal and spatial variability in rates.

Given that oxygen is the dominant electron acceptor in this plume and oxygen is likely available to both the source area and to the plume, the relative importance of mass loss in each segment was estimated. In Table 2.6 the mass of each compound lost up until sampling day 5140 was expressed as a percent of both the mass leached, as estimated by the mass flux at the fence 2.7 m downgradient of the source, and the initial mass in the source NAPL. In all cases the mass lost as a percent of mass leached is greater than the mass lost as a percent of the initial mass of the compound in the NAPL. The main factor for this is likely mass loss via biotransformation in the source zone. Note that the bulk of the oxygen available to the creosote source and plume passed through the source zone.

The mass lost as a percent of total mass for each organic compound was plotted against its respective  $\log K_{ow}$  value. The result was a linear relationship with a  $R^2$  value of 0.89, where the greatest percent mass loss is associated with the more water soluble compounds; a logical finding as by and large degradation occurs in the aqueous phase (Mueller et al., 1989). This result suggests that dissolution is an important control on mass lost at least in the source zone.

Table 2.7 contrasts the amount of apparent degradation occurring in the plume and source zone. The highly mobile compounds have a greater percent mass lost occurring in the plume while the biotransformation of highly retarded compounds appears to occur dominantly in the source zone. It appears the majority of the leached or dissolved mass for these retarded compounds does not appear to have even entered the plume. The higher rate of degradation of the more retarded compounds is likely because there is the same exposure of oxygen for all compounds in the source zone via background aerobic groundwater. Within the plume the availability of oxygen is higher for mobile compounds (low  $K_{ow}$ ) as highly retarded compounds remain within the depleted oxygen zone within the core of the plume.

In Figure 2.6 the mass degraded is represented by the area between the mass leached and total plume mass lines. The mass leached becomes a horizontal line when most if not all the mass has been removed from the source zone. As the mass in the plume becomes smaller degradation is exceeding leaching into the plume. For both carbazole and naphthalene (Figure 2.6a,b) almost all their mass has been removed from the source zone and significant degradation has been occurring.

By day 5140 some compounds like phenanthrene, 1-methyl naphthalene (Figure 2.6), acenaphthalene, and perhaps dibenzofuran have increasing plume mass and significant mass remaining in the source after day 5140 and as a result may extend further in the future. However, considerable biodegradation of these compounds is still occurring and removal of competing organic substrates should enhance biotransformation of these chemicals in the future. Our lack of understanding of the details of the biotransformation process adds some uncertainty about the future of these plumes. For example, will the Borden plume evolve into a dilute plume dominated by acenaphthalene as found at a former gasworks site (Zamfirescu & Grathwohl, 2001)? At actual contaminated sites this uncertainty about the biotransformation process adds uncertainty in the application of monitored natural attenuation.

Further research is required to confirm and understand biotransformation reactions occurring in such a complex chemical plume.

Table 2.6. A comparison of a compounds octanol-water partitioning coefficient to the mass loss as a percent of both the initial compound mass in the source NAPL and as a percent of the mass leached for that compound.

Compound	Log K <sub>ow</sub>	Initial Mass in the NAPL g	Mass Leached <sup>a</sup> up to day 5140 g	Mass in Plume on day 5140 g	Mass Lost <sup>b</sup> g	Mass Lost Compared to Mass Leached %	Mass Lost Compared to Initial Mass %
m-xylene	3.2	2849	2335	0	2335	100.0	82
naphthalene	3.3	7108	4813	107	4706	98	66
carbazole	3.72	242	111	41	70	63	29
1-m naphthalene	3.87	1415	471	57	414	88	29
acenaphthene	3.92	5260	872	182	690	79	13
biphenyl	3.98	1100	160	50	110	69	10
dibenzofuran	4.12	3237	462	176	286	62	9
fluorene	4.18	3760	225	59	166	74	4
anthracene	4.45	913	46	9	37	81	4
phenanthrene	4.46	9154	117	81	36	31	0.4

<sup>a</sup>Linear interpolation of mass flux values between synoptic monitoring events

<sup>b</sup>Mass leached minus the mass in plume

Table 2.7. Comparison of degradation occurring in the source zone and within the plume up to day 5140. The total amount of mass lost up to day 5140 compared to that which had dissolved or leached from the source NAPL is indicated in the final column.

Compound	Log $K_{ow}$	Mass on day 5140 (g)		Mass Lost (%)		Total dissolved mass degraded (%)
		Dissolved <sup>a</sup>	Entering Plume <sup>b</sup>	In Plume	In Source Plume	
m-xylene	3.2	2836	2335	0	18	82
naphthalene	3.3	6851	4813	107	30	69
carbazole	3.72	238	111	41	53	29
1-m naphthalene	3.87	585	471	57	19	71
acenaphthene	3.92	1983	872	182	56	35
biphenyl	3.98	416	160	50	62	26
dibenzofuran	4.12	1983	462	176	77	14
fluorene	4.18	1016	225	59	78	16
anthracene	4.45	121	46	9	62	31
phenanthrene	4.46	1184	117	81	90	3

<sup>a</sup>Based on the Raoult's Law model of source dissolution

<sup>b</sup>Based on the linear interpolation of mass flux data for a monitoring fence 2.7 m downgradient of source

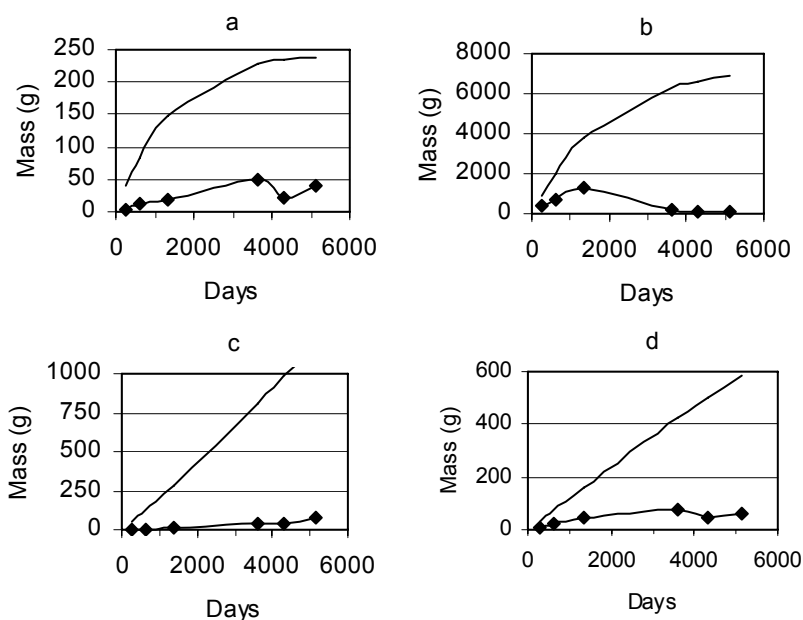


Figure 2.6. Mass leached (solid line) and total plume mass (line with data points) calculated versus time for (a) carbazole, (b) naphthalene, (c) phenanthrene and (d) 1-methyl naphthalene. The area between the mass leached and the total plume mass lines represents mass that is assumed to have been degraded.

## Chapter 3

### Partial Chemical Oxidation of an Emplaced Creosote Source

Due to low solubilities residual NAPL at contaminated sites often leaves relentless plumes of dissolved compounds emanating from the source. *In situ* chemical oxidation (ISCO) attempts to increase the rate of mass removal from the source and thus decrease the time span of these emanations. There is no above ground water treatment or disposal system required and ISCO is capable of treating the NAPL, soil and groundwater contamination simultaneously. The use of ISCO as a remediation strategy has been commonly explored for dissolved chlorinated solvents (Schnarr et al, 1998; Yan & Schwartz, 1999; McKay et al., 2000; Mott-Smith et al, 2000; MacKinnon & Thomson, 2002; Amine Dahmani et al., 2006), hydrocarbons (Martens & Frankenberger, 1995; Leethem, 2002; Nadarajah et al., 2002; Millioli et al., 2003), and coal tar or creosote (Gates-Anderson et al., 2001; Nam et al, 2001; Brown et al., 2002; Mueller et al., 2006).

ISCO often involves flushing a residually contaminated area with a reactive solution or oxidant. The oxidant reacts to break down the contaminants in the dissolved phase. This in turn increases the rate of mass transfer from the NAPL to the water phase. As a result the contaminant residual mass and the flux of contaminants downgradient into the groundwater plume are reduced. Various oxidants can be used depending on the contaminant and aquifer properties (Amarante, 2000; Gates-Anderson, 2001). Common options include Fenton's reagent, persulfate and permanganate.

Fenton's reagent is a mixture of hydrogen peroxide and ferrous iron that produce hydroxyl free radicals, a powerful oxidant. Fenton's reagent is popular because it is an oxidant that degrades a wide variety of organic contaminants (Watts & Teel, 2006) and the chemicals are readily available and inexpensive (Amarante, 2000). The oxidant works best when pH is low. The use of Fenton's reagent as an oxidant is limited by the decomposition of hydrogen peroxide which is rapid in the subsurface (Watts & Teel, 2006). This is especially true for soils containing carbonate, bicarbonate and organic matter which create competing reactions with Fenton's reagent (Amarante, 2000).

Persulfate is an oxidant that has only more recently been explored and therefore less is known (Amine Dahmani et al, 2006). Persulfate is commonly activated thermally or with ferrous iron to create sulfate free radicals (Liang et al, 2004). It reacts with many compounds and is more stable than Fenton's reagent in the subsurface (Watts & Teel, 2006), permitting transport to residuals from injection wells. Persulfate oxidation rates are pH sensitive with low conditions preferred (Leethem, 2002).

Potassium permanganate ( $\text{KMnO}_4$ ) is a popular oxidant because of its high solubility which allows for a significant load of oxidant to be delivered to the contaminated zone, its low cost, and ease of handling (Schnarr et al., 1998). It can be applied in aquifers of high carbonate or bicarbonate content and is effective over a wide range of pH (Amarante, 2000; Schroth et al., 2001; Watts & Teel, 2006). Permanganate is more persistent than other reagents *in situ* however it is not able to breakdown as wide a variety of contaminants as the powerful hydroxyl and sulfate free radicals. Permanganate is an effective oxidant for chlorinated solvents as well as alkenes, phenols, sulfides and certain polycyclic aromatic hydrocarbons (PAH's). It is limited in its ability to oxidize other common contaminants such as petroleum hydrocarbons (Amarante, 2000; Leethem, 2002; Forsey, 2004).

PAH's are common contaminants in the subsurface with a vast range of chemical/physical properties. Fenton's reagent and persulfate are commonly applied as an oxidant to the lighter PAH's such as BTEX (Hoag et al., 2006). Permanganate generally has been overlooked until recent years for *in situ* oxidation of PAH's. This is likely due to permanganate's inability to oxidize BTEX (Brown et al., 2002). New studies show that permanganate can be effective in breaking down the higher molecular weight PAH's, like anthracene and naphthalene, associated with coal tar creosote (Brown et al., 2002; Forsey, 2004; Mueller et al, 2006).

When  $\text{KMnO}_4$  is flushed through the contaminated aquifer organic compounds are oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , and  $\text{KMnO}_4$  is reduced to  $\text{MnO}_2(\text{s})$  (Schnarr et al, 1998). Mueller et al. (2006) completed an ISCO pilot field test of creosote residuals with

KMnO<sub>4</sub>. They found the mass was reduced by 10 to 79% and the flux of contaminants was reduced by 56 to 99%. Overall the lighter molecular weight PAH's had a greater relative mass reduction in soil concentrations whereas a greater relative flux reduction (dissolved concentrations) was observed for the higher molecular weight compounds. Mueller et al. also found that with the significant removal of contaminants from the NAPL the viscosity increased resulting in stabilization of the source NAPL.

Gates-Anderson et al. (2001) conducted batch tests comparing the treatment efficiency of KMnO<sub>4</sub> and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). In a sandy soil KMnO<sub>4</sub> was able to reduce all PAH concentrations by 99% (naphthalene, phenanthrene and pyrene) whereas H<sub>2</sub>O<sub>2</sub> had little effect. It was only when the pH of the sandy soil was adjusted to 3 that H<sub>2</sub>O<sub>2</sub> was able to oxidize the PAHs. Even then H<sub>2</sub>O<sub>2</sub> was not as effective as KMnO<sub>4</sub> for phenanthrene and pyrene. In a clay soil H<sub>2</sub>O<sub>2</sub> amended with Fe(II) (Fenton's reagent) performed equally as well as KMnO<sub>4</sub>. Overall Gates-Anderson et al. found the treatment efficiency of H<sub>2</sub>O<sub>2</sub> dependent on the type of contaminant and soil whereas KMnO<sub>4</sub> was more consistent under all conditions studied.

Brown et al. (2003) demonstrated through batch tests a reduction in soil sorbed concentrations for a mixture of six PAH's using KMnO<sub>4</sub>. The greatest reductions in soil concentrations were observed for benzo(a)pyrene (72.1%), pyrene (64.2%), phenanthrene (56.2%) and anthracene (53.8%). Fluoranthene and chrysene were more resistant to oxidation with only 13.4% and 7.8% reduction in soil concentrations respectively. Brown et al. concluded that the PAH's are likely not completely mineralized by KMnO<sub>4</sub> oxidation reactions but their structure is altered enough to provide great improvement in aqueous solubility and availability for natural biotic mineralization.

Application of ISCO using permanganate can be limited by the formation of solid precipitates (MnO<sub>2</sub>(s)) and CO<sub>2</sub> gas, both leading to drastic pore space reduction which results in a reduced hydraulic conductivity (K) of the aquifer. A reduction in hydraulic conductivity can result in significant delivery problems. Li and Schwartz (2004) found the rapid build up of these reaction by-products reduced K by as much as 80% in a laboratory column. Schroth et al. (2001) conducted column experiments evaluating the effect of *in situ* TCE oxidation by KMnO<sub>4</sub> on porous medium hydraulic properties.

During the first 24 hours of the experiment CO<sub>2</sub> gas production and MnO<sub>2</sub> precipitation were observed visually and K was found to be reduced by 96%. The use of a buffered KMnO<sub>4</sub> solution reduced the decrease in K to 53%. The buffered solution was effective at maintaining the pH in the weakly buffered system (silica sand) and therefore decreasing the formation of CO<sub>2</sub> gas bubbles which contributed to the reduced K.

ISCO is becoming a cost effective solution to decreasing the life time of residual NAPL sources. Permanganate oxidizes the reactive compounds in the dissolved phase which increases the rate of mass transfer from the NAPL to the water phase (Mueller et al., 2006). Therefore permanganate directly breaks down contaminants in the dissolved phase which indirectly decreases the mass of contaminants of reactive compounds in the residual NAPL. The compounds are treated and removed at a higher rate. Once the treatment has ceased the reactive compounds have a decreased mole fraction in the residual NAPL and thus their flux from the NAPL is subsequently decreased as per Raoult's Law. The reduced flux results in dissolved plumes that natural attenuation processes are more capable of handling (Mueller et al., 2006). In contrast, rapid removal of reactive compounds from the residual NAPL increases the mole fraction of the non-reactive or slowly reactive compounds and, as per Raoult's Law, causes higher aqueous concentrations of these compounds in the source zone. While ISCO may also shorten the lifetime of the residual source, it may also increase the flux of non-reactive (with permanganate) compounds into the downgradient groundwater.

Forsey (2004) conducted a laboratory and numerical investigation of the *in situ* chemical oxidation of creosote/coal tar residuals. This investigation led to a short-term, field scale evaluation of ISCO of a small emplaced coal tar creosote source within the sandy Borden research aquifer by Lamarche (2002). The longer term impact on the dissolved organic plumes is the subject of this paper.

The dissolved plumes of organic contaminants emanating from the coal tar creosote source have been well documented over the past 14 years (King & Barker, 1999; King et al, 1999; Fraser et al, in submission). This has provided an analysis of the long



term behaviour of ten coal tar creosote compounds prior to the *in situ* chemical oxidation of the source. The plume has been monitored extensively on two occasions since then. This detailed data set provides the opportunity to assess the impact of the source zone oxidation on the dissolved phase of contaminants in terms of extent and distribution, mass discharge of contaminants entering the plume and the total mass of chemicals in the plume.

### 3.1 Laboratory Investigations

#### 3.1.1 Reactivity of Creosote Compounds with Permanganate

Forsey (2004) conducted batch and column experiments to assess the ability of  $\text{KMnO}_4$  to oxidize creosote compounds and to increase their NAPL-to-water mass transfer rates. The experiments were designed to investigate the feasibility of using permanganate as an *in situ* remediation technology for the removal of creosote compounds at the CFB Borden research site.

The batch experiments were conducted over a 27 day period with 15 additions of the oxidant. Initially, 0.1 mL of creosote was added to 1 L 0.01 M phosphate-buffered, organic-free water with a pH of 7 and stirred for 2 days. This allowed the NAPL and water to equilibrate prior to the addition of permanganate. The permanganate was then added (1:1 molar ratio of reagent to creosote) daily for the first 5 days and then every other day for the next 22 days. Forsey observed the more soluble compounds such as phenol, p-cresol, m-xylene and indole were removed from the aqueous phase within the first 2 to 15 days of the addition of permanganate. Less soluble compounds were oxidized to very low aqueous concentrations over the course of the experiment. Phenanthrene, dibenzofuran, biphenyl and fluoranthene saw the least reduction in aqueous concentrations (<50%). However, by the end of the experiment greater than 50% of the mass of even these compounds had been removed from the oil phase.

The batch experiments demonstrated that  $\text{KMnO}_4$  was able to reduce the mass of the creosote compounds within the NAPL. Forsey determined that oxidation occurs mainly in the aqueous phase or on the surface of the NAPL, reflecting permanganate insolubility in hydrophobic liquids like creosote. Forsey concluded that the rate of removal of creosote compounds from a contaminated site will depend on the rate of oxidation and also the rate of dissolution from the oil phase.

With an understanding of the reactivity of the creosote compounds Forsey then conducted column experiments using Borden aquifer material with creosote at 3% saturation. The column was flushed with 1.8 L of  $\text{KMnO}_4$  solution (15 g/L  $\text{KMnO}_4$ ) with

a volumetric flow rate of  $3.59 \times 10^{-4} \text{ m}^3/\text{day}$  over a period of 5 days. The added  $\text{KMnO}_4$  was reduced to visible manganese oxides and preferred pathways developed in the column. With each addition of  $\text{KMnO}_4$  Forsey observed the pink permanganate solution to diffuse into pore spaces that were initially bypassed. By the 6<sup>th</sup> injection the sand was completely covered with manganese oxides making it difficult to observe movement of the permanganate solution through the porous media. Over 5 days 1.8 L of  $\text{KMnO}_4$  flushing decreased the initial mass of creosote compounds by 56% compared to the control column (water flushing only) where only 8% was removed.

Forsey's column experiments revealed a significant increase in the mass transfer rates of readily oxidizable compounds such as pyrene and naphthalene when  $\text{KMnO}_4$  was applied. An increase in the rate of mass removal for non-oxidizable compounds such as dibenzofuran and biphenyl was also noted. The enhanced dissolution of these non-oxidized compounds was attributed to an increase in their mole fractions in the NAPL due to the rapid removal of more oxidizable compounds as per Raoult's Law. Table 3.1 summarizes the results of these column experiments.

Forsey (2004) also determined the second-order rate constants for naphthalene, phenanthrene, chrysene, pyrene, 1-methyl naphthalene, 2-methyl naphthalene, acenaphthene, fluorine, carbazole, isopropylbenzene, ethylbenzene and methylbenzene (listed in Table 3.1) and related trends in reactivity to bond dissociation energies, ionization potentials and calculated heats of formation. The rate of oxidation of PAH's increased as the number of aromatic rings increased. Forsey found that fluoranthene was only partially oxidized by  $\text{KMnO}_4$  and the rate of oxidation of anthracene was too fast to be measured. He also found that compounds such as biphenyl, dibenzofuran, benzene and tert-butylbenzene with stable aromatic ring systems and the absence of benzylic hydrogens were resistant to oxidation.

Table 3.1. Summary of oxidation during column experiments of Forsey (2004). Control column ran for 6.29 days with a flow rate of  $1.41 \times 10^{-3} \text{ m}^3/\text{day}$  (77.5 pore volumes). Treated column ran for 5.04 days with a flow rate of  $3.59 \times 10^{-4} \text{ m}^3/\text{day}$  (19.01 pore volumes) and a  $\text{KMnO}_4$  concentration of 15 g/L. Second-order rate constants ( $K_C$ ) for selected creosote compounds determined by Forsey (2004) are also listed. The uncertainties specified reflect the 95% confidence level.

Compound	Second Order Average Rate Constant ( $K_C$ ), ( $\text{M}^{-1}\text{s}^{-1}$ )	Control			Treated		
		Initial Mass (mg)	Final Mass (mg)	% Removed	Initial Mass (mg)	Final Mass (mg)	% Removed
benzene	NR <sup>a</sup>				NR in batch <sup>b</sup>		
methylbenzene	$5.3 \times 10^{-4} \pm 5 \times 10^{-4}$				NA <sup>c</sup>		
ethylbenzene	$6.0 \times 10^{-3} \pm 8 \times 10^{-4}$				NA <sup>c</sup>		
isopropylbenzene	$6.2 \times 10^{-3} \pm 2 \times 10^{-3}$				NA <sup>c</sup>		
naphthalene	$1.1 \times 10^{-2} \pm 2 \times 10^{-3}$	279	128	54	326	55	83
t-butylbenzene	NR <sup>a</sup>				NR in batch <sup>b</sup>		
1-methyl naphthalene	$1.4 \times 10^{-2} \pm 2 \times 10^{-3}$	57	50	12	72	28	60
2 methyl naphthalene	$1.8 \times 10^{-2} \pm 3 \times 10^{-3}$				NA <sup>c</sup>		
biphenyl	NR <sup>a</sup>	47	41	13	60	50	17
acenaphthene	$0.21 \pm 3 \times 10^{-2}$	218	210	4	277	41	85
fluorene	$0.43 \pm 3 \times 10^{-2}$	171	170	0.3	215	34	84
carbazole	$0.44 \pm 8 \times 10^{-2}$	33	23	30	46	9	81
dibenzofuran	NR <sup>a</sup>	177	172	3	246	209	15
phenanthrene	$0.42 \pm 3 \times 10^{-2}$	404	418	-4	548	252	54
anthracene		48	46	3	40	2	96
pyrene	$1.7 \pm 0.6^d$	155	155	-0.2	202	103	49
fluoranthene	$0.9 \pm 0.3^d$	189	202	-7	252	201	20
chrysene	$1.2 \times 10^{-2} \pm 1 \times 10^{-2}^d$	39	40	-3	38	32	17
Total		1815	1655	9	2321	1016	56

<sup>a</sup>No reaction

<sup>b</sup>Compound was not analysed in the column experiment but was observed not to react with permanganate in batch tests.

<sup>c</sup>Compound was not analysed in column experiments

<sup>d</sup>Second-order constant has been tentatively assigned, refer to Forsey (2004)

## 3.2 Field Experiment

### 3.2.1 Field Site

The coal tar creosote source in the sandy Borden research aquifer has been the subject of numerous investigations (King & Barker, 1999; King et al., 1999; Fraser et al, in submission) since its emplacement in 1991. The source zone consists of 2 blocks which measure 1.5 m deep, 2 m wide (perpendicular to groundwater flow) and 0.5 m thick. They were formed *in situ* by adding coarse sand mixed with creosote at about 3% residual saturation. The two blocks were placed 1 m apart and from 2 to 3.5 m bgs (> 1 m below the water table). Details are provided by King & Barker (1999). The unconsolidated sand aquifer has a hydraulic conductivity of approximately  $8 \times 10^{-5}$  m/s and groundwater flows horizontally at about 0.09 m/day.

A dense monitoring network consisting of ~280 14-point, multilevel monitors has allowed the plumes of dissolved compounds emanating from the source to be examined in detail over the past 16 years. For this particular field study major groundwater sampling events have occurred on 278 (King, 1997), 626 (King, 1997), 1357 (King, 1997), 4315 (Fraser, 2005) and 5140 (this study) days since source emplacement. Each sample event represents a 1 to 4 week period where 700 to 2700 samples were collected and analysed for: phenol, m-xylene, naphthalene, 1-methyl naphthalene, acenaphthene, biphenyl, phenanthrene, anthracene, dibenzofuran, fluorene and carbazole (Appendix A). Phenols and monoaromatics had already been leached and degraded before the ISCO and are not discussed here (refer to King & Barker, 1997). In addition, on day 4065 (Lamarche, 2002) only the monitoring fence 2.7 m downgradient of the source was sampled for the above compounds.

### 3.2.2 Application of Permanganate

In the fall of 2001 Lamarche (2002) completed an ISCO of the coal tar creosote source zone using a semi-passive delivery system. The purpose of the oxidation was to partially remediate the source zone to reduce the flux of contaminants into the dissolved plume and permitting natural attenuation to further reduce the plume extent. A total of 6 pulse injections were undertaken over a 35 day period (Day 3675 to 3710). Each injection was

designed to evenly split 3.2 m<sup>3</sup> of 15 g/L KMnO<sub>4</sub> solution between four upgradient injection wells (~0.3 m upgradient of source), with injection at a rate of 5 L/min over 10 hours.

After the first injection decreased hydraulic conductivity made it difficult to deliver the designed amount of KMnO<sub>4</sub> solution. Attempts were made to combat the decreased injection rate by increasing the gradient after the first injection (by extending the injection well tubing above ground) as well as by installing new injection wells prior to the fifth injection. In the end, the decreased hydraulic conductivity, attributed to MnO<sub>2</sub>(s) formation, caused local mounding of the water table upgradient of the source and consequently each injection episode fell short of the designed volume. Overall 125 kg of KMnO<sub>4</sub> was delivered to the source zone by the 6 pulsing events with an average injected KMnO<sub>4</sub> concentration of 13 g/L and an average volume per episode of 1.96 m<sup>3</sup>.

### **3.2.3 Short Term Effects of ISCO**

Lamarche (2002) examined the short term effects (~8 months) of the ISCO of the creosote source using PAH concentrations and mass discharge estimates. The dissolved PAH concentrations were measured at a fence line 0.3 m downgradient of the source prior to, during and post-oxidation. Lamarche found a general trend of higher total PAH reductions in areas of higher permanganate concentrations.

The ambient mass discharge (AMD) was estimated by spatially integrating the 0.3 m monitoring fence data and applying a flux of 5.4 and 4.4 cm/day for pre- and post-treatment AMD calculations. The Darcy flux values were determined from water level measurements on the day of sampling and an average hydraulic conductivity of  $7 \times 10^{-5}$  m/s (Mackay, 1986). The total PAH load decreased after oxidation from about 2100 mg/day to 1100 mg/day. An approximate 40% reduction or greater in AMD was observed for acenaphthene, pyrene, naphthalene, 1-methyl naphthalene, acenaphthylene, anthracene, carbazole, fluorine and phenanthrene, but only 15% for both biphenyl and dibenzofuran.

A forced gradient mass discharge test (FGMD) was also conducted pre- and post-treatment. The FGMD involved extracting groundwater downgradient of the source and sampling the effluent over the course of 8 days. The total PAH load in the post-treatment

effluent decreased by <20%. The majority of compounds did not show a significant change in mass discharge except for carbazole which had a 55% decrease in mass discharge post oxidation. Results of both the AMD and FGMD are summarized in Table 3.2.

Coring of the source zone revealed a very heterogeneous creosote distribution but no statistically significant change in PAH concentrations post-treatment. Inspection of the core material pre- and post-treatment revealed a change in colour from grey to black. Chemical analysis revealed an increase in manganese content.

Overall the short term effect of the ISCO was a decrease in PAH mass discharge, excepting biphenyl and dibenzofuran, emanating from the creosote source. The most significant decreases were for compounds found to be most reactive with respect to permanganate.

Table 3.2. Summary of ambient mass discharge (AMD) and forced gradient mass discharge (FGMD) measurements taken pre- and post-treatment by Lamarche (2002).

Compound	AMD (mg/day)		FGMD (mg/day)	
	Pre-treatment	Post-treatment	Pre-treatment	Post-treatment
naphthalene	748	311	3080	2580
1-methyl naphthalene	199	116	855	777
acenaphthylene	14	6	61	39
biphenyl	84	71	384	434
acenaphthene	433	196	2040	1470
fluorene	114	51	648	425
carbazole	60	18	426	192
dibenzofuran	252	215	1220	1270
phenanthrene	95	60	529	530
anthracene	31	14	139	111
pyrene	8	3	45	30
fluoranthene	12	11	61	83
Total	2060	1070	9490	7940

### 3.2.4 Longer-Term Effects

#### 3.2.4.1 Assessment Approaches

The pre- and post-oxidation dissolved plumes were compared using three metrics: size, total mass and mass discharge into the plume. Plume dissolved concentration contours were created using the maximum concentration of a compound detected at each multilevel sampler. Results are shown in Figure 3.1. Pre-oxidation data from days 1357 and 3619 and post-oxidation data from days 4315 and 5140 provide a qualitative view of the plume extents.

The total mass in each plume was calculated for each sampling day as the sum of the dissolved and sorbed masses of each compound and is shown in Figure 3.2. The dissolved mass ( $M_D$ ) was calculated for a sampling event using a three-dimensional integration of the contaminant concentrations (King et al, 1999). The sorbed mass ( $M_S$ ) was estimated with the retardation factor ( $R$ ) according to:

$$M_S = (R-1)M_D \quad (3.1)$$

Retardation values were calculated using distribution coefficients ( $K_d$ ), a porosity of 0.33 and a bulk density of 1.81 g/cm<sup>3</sup>. Distribution coefficients for dibenzofuran, carbazole, 1-methyl naphthalene, naphthalene and phenanthrene were determined directly through laboratory batch testing by King et al (1999). Anthracene, biphenyl, acenaphthene, fluorine and xylene were not considered in the batch tests as a result empirical correlation of literature values of  $K_{oc}$  with  $K_{ow}$  (Fraser et al., in submission) were used to determine  $K_d$ .

The mass discharge of each compound entering the plume was measured at a detailed monitoring fence 2.7 m downgradient of the source. This monitoring fence has been augmented over the years. On sampling days 278, 626 and 1357 the fence consisted of 8 multilevels with 14 vertical sampling points. For days 3619, 4315, 4065 and 5140 the fence was increased to 15 wells with the majority spaced at 0.5 m and each with 14 vertical sampling points. The fence was divided into individual polygons centered on



each sampling point. The boundary of each polygon extended half way to the neighboring sampling point. The chemical discharge for the polygon was calculated as the area of the polygon multiplied by the concentration at the sampling point and the groundwater flux (0.3 m/day). The mass discharge for the fence is the sum of the discharges for each individual polygon. Figure 3.3 displays the mass discharge of each compound over time.

Error bars on Figure 3.2 and Figure 3.3 reflect the estimated relative error in mass discharge and total plume mass calculations. Fraser et al. (in submission) estimated the uncertainty associated with the mass discharge and total plume mass calculations performed with this data set. The total relative uncertainty in the mass discharge is dependent on the uncertainty in groundwater flux, chemical analysis and monitoring density. Fraser et al. determined that the relative uncertainty (1 SD) for mass discharge on days 278, 626 and 1357 should not exceed 28%, while the uncertainty should approach 12% for the other days. The difference in relative error is due to the augmented sampling density for the later days. The components of uncertainty for total plume mass include analytical and monitoring uncertainty associated with dissolved mass as well as the uncertainty in the estimation of sorbed mass. Refer to Fraser et al. (in submission) for a full discussion.

To understand the impact that the oxidation would have on the plumes of organics it is important to estimate the amount of NAPL remaining in the source zone at the time of the oxidation. Coring of the source during this study revealed the PAH distribution to be highly variable (Lamarche, 2002), despite mixing of the NAPL at less than residual concentrations with coarse sand to homogenize the source before installation (Malcolmson, 1992). Therefore coring and chemical analysis provides only a highly uncertain estimate of the mass of compounds in the NAPL residual.

King & Barker (1999) used Raoult's Law to model the source dissolution over time and found the model to conform with dissolved concentrations in the source within a factor of 2. Fraser et al. (in submission) extended this model to 5140 days (latest

sampling date) since source installation and included 19 compounds initially analysed by Malcolmson (1992) at the time of installation (Appendix B). The model adequately predicted the dissolution of 9 of 11 compounds from the emplaced coal tar creosote residual source. The model assumed a specific groundwater flux of 0.03 m/day and a source zone cross-sectional area of 6 m<sup>2</sup> perpendicular to groundwater flow. Figure 3.3 displays a solid line representing the mass discharge as predicted by the Raoult's Law model of source dissolution. As explained in Fraser et al (in submission) the measured mass discharge is less than that predicted by the model, in large part due to significant biodegradation occurring in the source and before the mass discharge monitoring fence 2.7 m downgradient of the source.

The model estimates that on day 3675 (start of oxidation) there was approximately 350 moles of creosote compounds remaining in the source zone. Approximately 790 moles of permanganate was delivered under natural gradient conditions. The natural oxidant demand (NOD) of the aquifer is  $2.21 \times 10^{-3}$  mol/kg (Mumford et al., 2005) as a result it was estimated the aquifer would consume at most 45 moles of permanganate. Therefore about 745 moles of permanganate is expected to have been delivered to the source zone. Using an average stoichiometric ratio of 1:18.6 for permanganate reactivity with organics, suggests that 40 moles of creosote compounds or 11% of the source zone could have been oxidized.

#### **3.2.4.2 The Effect of the ISCO: Qualitative Trends**

The pre-oxidation trends are based on days 278, 626, 1357 and 3619 and the post-oxidation trends include sample days 4065, 4315 and 5140. Four representative compounds are described in detail: carbazole, anthracene, biphenyl and dibenzofuran (Results for all compounds studied can be found in Appendix B).

The pre-oxidation trends of the oxidizable compounds, carbazole and anthracene, are increasing plume size (Figure 3.1a,c) and plume mass (Figure 3.2a,b). The pre-oxidation mass discharge of carbazole peaked on day 626 and has remained relatively constant while anthracene continued increasing (Figure 3.3a, b).

Maximum concentrations within the carbazole plume decreased on day 4315 (post-oxidation) however, plume size remained the same. The plume mass and mass

discharge decreased on day 4315 compared to pre-oxidation values. By day 5140 dissolved plume concentrations, total plume mass and mass discharge values had returned to pre-oxidation values.

Anthracene is unique in that it is the only compound that has shown a continued decreasing post-oxidation trend for plume extent, plume mass, and influx into the plume. On day 4315 the high concentrations in the core of the anthracene plume had decreased. By day 5140 the size of the dissolved anthracene plume had shrunk and the plume mass was decreasing. Mass discharge of anthracene into the plume showed a clearly decreasing trend post-oxidation.

The majority of the remaining reactive compounds behave as did carbazole (see Table 3.3 and Table 3.4). Acenaphthene, 1-methyl naphthalene, phenanthrene and fluorine all in some way displayed one or more effect of the oxidation initially, generally an initial decrease in plume mass and/or mass discharge for day 4065 and/or 4315. However, like carbazole, plume mass and mass discharge had returned to pre-oxidation values or higher by day 5140. Naphthalene and m-xylene were undergoing significant attenuation at the time of oxidation and consequently it is not possible to separate the effects of the oxidation from that of the ongoing natural attenuation.

The non-permanganate-oxidizable compounds followed in this study are biphenyl and dibenzofuran. Pre-oxidation, these compounds were showing increasing plume size and total plume mass. Mass discharge of biphenyl into the plume peaked on day 626 then remained relatively consistent while dibenzofuran continued to increase. Post-oxidation, on day 4315, both compounds show a general decrease in concentrations within the core of the plume. Total plume mass appears to have decreased on this day, however, this is within the data uncertainty. Mass discharge measured on day 4065 showed a decline in both biphenyl and dibenzofuran mass emanating from the source. By day 5140 total plume mass and mass discharges returned to or were greater than pre-oxidation values.

The plume mass was broken down into 32, approximately 1 m slices with increasing distance from the source. The dissolved mass in a plume typically decreases

with increasing distance from the source due to dispersive dilution and biotransformation processes. Figure 3.4 then shows the longitudinal distribution of the dissolved mass for days 3619, 4315 and 5140. Figure 3.4 also shows the approximate location of the dissolved compounds that left the source with the water over the 35 day *in situ* oxidation period. This was calculated for both days, based on advection (groundwater velocity of 9 cm/day) and retardation. It can be expected that the organics dissolved in this slug of treatment water were oxidized and thus are migrating at reduced concentration. Therefore, a significant decrease in dissolved mass is expected in this zone.

Carbazole is readily oxidized by permanganate therefore its plume would have been expected to have a section with decreased mass. On day 4315, using a retardation value of 5.6 (Fraser et al., in submission, Table 1), carbazole would have traveled about 10 m since the time of oxidation (Figure 3.4a). While the mass within this area of the carbazole plume is at its greatest, just upgradient (<10 m) there is a decrease in mass. By day 5140 the slug of water that carbazole occupied at the time of oxidation would be at about 23 m. This is on the very edge of the carbazole plume where contaminant concentrations are decreasing, becoming non-detectable by around 28 m from the source zone. Thus, there may have been a significant, short-term reduction of carbazole emanating from the source due to the ISCO.

Anthracene is highly retarded (Fraser et al., in submission, Table 1), and as a result by day 4315 the oxidized slug of anthracene had not yet entered the monitoring network (~3.0 m from the source). On day 5140 the oxidized section of the anthracene plume was expected to be centred approximately 6.5 m downgradient of the source. In Figure 3.4b the low mass of anthracene in this section is observed. Thus, this low mass of anthracene occupying the area where the treated water was expected to be centred indicates at least a short term effect of the *in situ* oxidation.

Biphenyl is non-reactive with permanganate with a retardation value of 7.5 (Table 2.1). By day 4315 dissolved biphenyl emanated during ISCO would have traveled about 7.5 m from the source. Between 3 and 11 m there is a decrease in mass and it is within this area (7.5 m) that the affected biphenyl would be located. Because biphenyl is non-

oxidizable this decrease in mass coincident with the location of the treated water could be a result of reduced flux of biphenyl during and immediately following the oxidation due to inhibited mass transfer from the NAPL to the aqueous phase. Another possibility for a reduced flux of biphenyl is a decreased water flux through the source zone resulting from a lowered hydraulic conductivity from reaction by products.

On day 4315, using a retardation value of 4.7 (Fraser et al, in submission, Table 1), the slug of dibenzofuran that emanated from the source during the oxidation would be around 11 m. This corresponds to a peak in mass within the plume. The post-oxidation area of the plume (<11 m) shows a dip in the mass distribution. By day 5140 the dissolved dibenzofuran slug associated with the oxidation would have migrated around 28 m and this is beyond the detected dibenzofuran plume.

All four compounds seem to show a decrease in mass on day 4315 within or just after the area that compound would have occupied. Since both oxidizable and non-oxidizable compounds show this effect one would initially conclude the mass transfer of the compounds from the NAPL to the aqueous phase may have been inhibited. However, upon further observation of the longitudinal distribution of the compounds on sample day 5140 it appears this decrease in mass around the 5 to 10 m distance from the source persists. It is not clear why this area of the plume shows a dip in mass on both sample days within the same area of the plume. The entire plume was encapsulated by the monitoring network, therefore essentially all chemical mass discharge was likely accounted for. However, the density of points (4 to 8 points/m<sup>2</sup>) suggests a relative uncertainty of > 10% in mass estimate, but without bias (Béland-Pelletier, in submission). This ongoing dip in mass 5 to 11 m downgradient of the source could be a result of ongoing mass transfer reduction due to the ISCO. Given the associated uncertainty, this suggestion remains tentative.

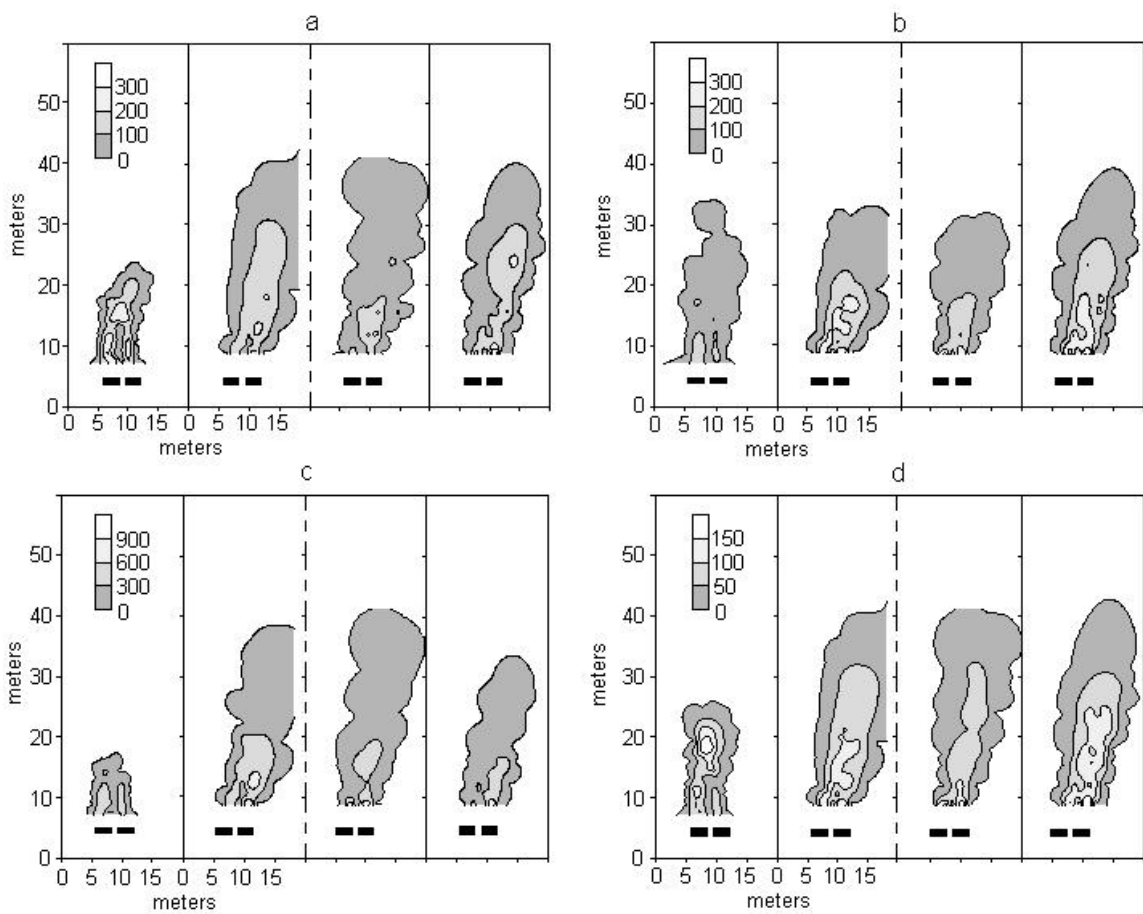


Figure 3.1. Plan view contour plots of (a) carbazole, (b) dibenzofuran, (c) anthracene and (d) biphenyl. Shown from left to right as 1357, 3619, 4315 and 5140 days since source emplacement. The *in situ* oxidation occurred from day 3675 to day 3710 and is represented by the dashed vertical axis.

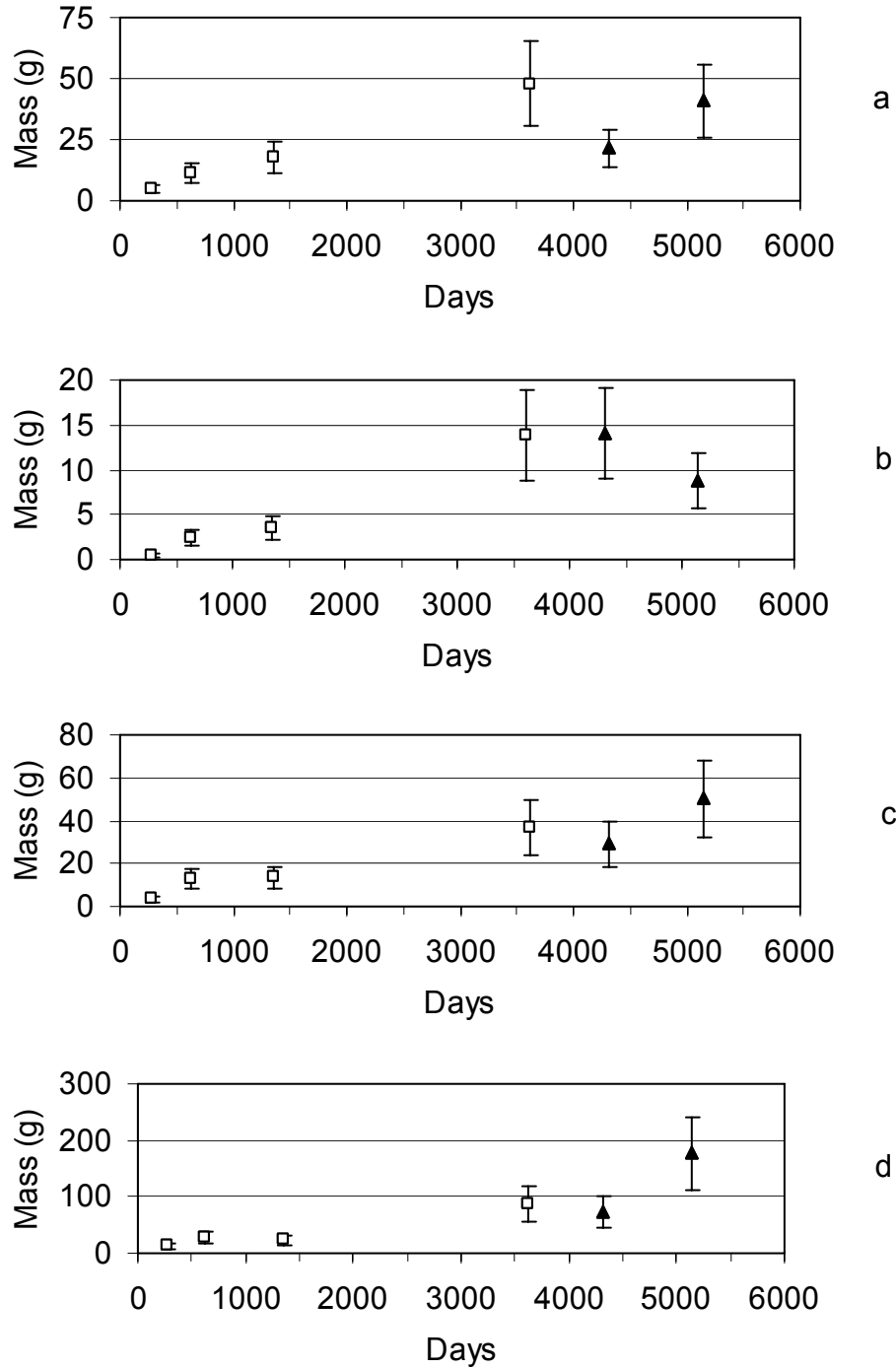


Figure 3.2. Total plume mass (dissolved and sorbed) calculated for (a) carbazole, (b) anthracene, (c) biphenyl and (d) dibenzofuran. Error bars are dependent on  $K_{ow}$  value of compound and therefore greatest estimated percent error of 36 is shown. Squares represent pre-oxidation and triangles represent post-oxidation.

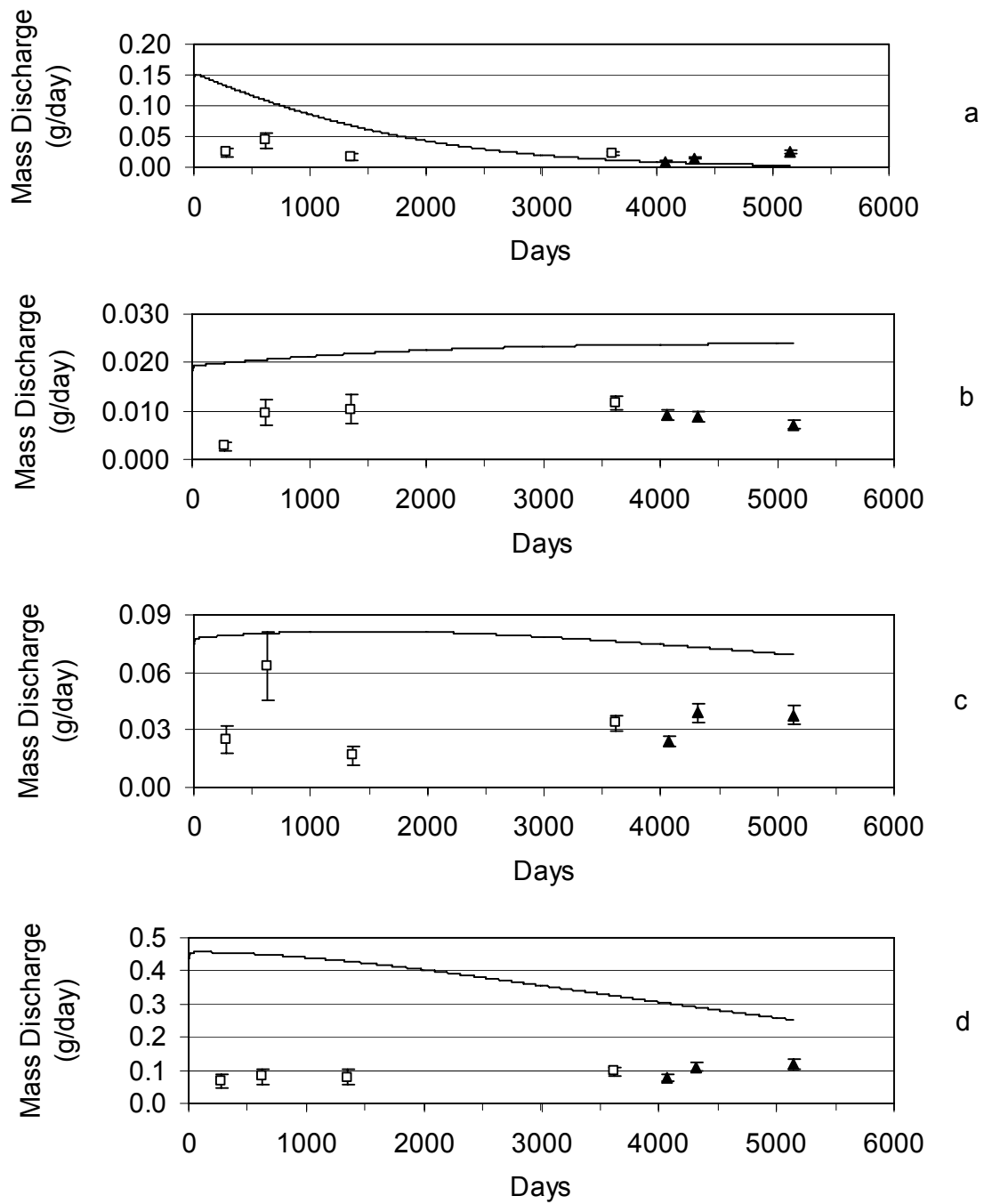


Figure 3.3. Mass discharge of (a) carbazole, (b) anthracene, (c) biphenyl and (d) dibenzofuran. Solid line represents mass discharge predicted by Raoult's Law Model and data points represent mass discharge calculated at monitoring fence. Days 278, 626 and 1357 have 28% error bars all other days have 12% error bars. Squares represent pre-oxidation triangles represent post-oxidation.



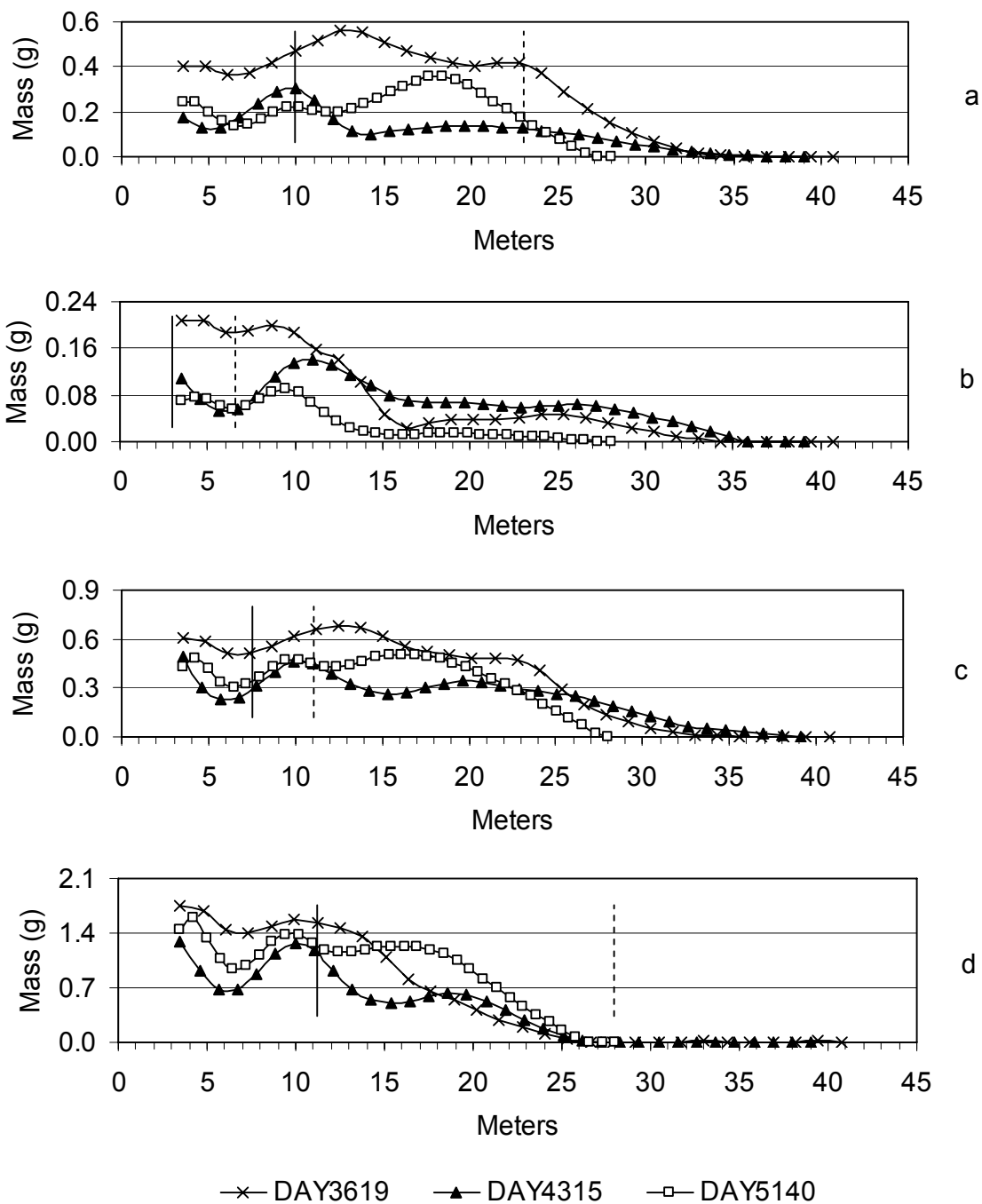


Figure 3.4. Mass distribution of dissolved (a) carbazole, (b) anthracene, (c) biphenyl and (d) dibenzofuran for pre-oxidation day 3619 and post-oxidation days 4315 and 5140. Vertical lines represent distance compound traveled based on advection and retardation for day 4315 (solid line) and 5140 (dashed line). By day 4315 the injected slug of permanganate would have migrated beyond the monitoring network.

Table 3.3. Total plume mass (g) calculated for each compound for a given sampling day. Dotted vertical line represents time of oxidation (day 3675 to day 3710).

Compound	Sample Day					
	278	626	1357	3619	4315	5140
m-xylene	580	230	92	4.4	0.9	0
naphthalene	410	750	1300	220	110	110
1-methyl naphthalene	11	22	42	75	45	57
biphenyl	3.5	13	14	37	29	50
acenaphthene	18	31	64	170	130	180
fluorene	2.4	7.1	-	40	31	59
carbazole	4.5	11	18	48	21	41
dibenzofuran	14	28	24	88	73	180
phenanthrene	0.31	1.1	8.0	35	40	81
anthracene	0.5	2.4	3.5	14	14	8.8

- no data reported for fluorene on sample day 1357

Table 3.4. Total mass discharge (g/day) of each compound for a given sampling day. Dotted vertical line represents time of oxidation (day 3675 to day 3710).

Compound	Sample Day						
	278	626	1357	3619	4065	4315	5140
m-xylene	3.0	1.0	0.28	0.0040	0.0033	0.013	0
naphthalene	2.8	2.2	1.1	0.34	0.22	0.24	0.16
1-methyl naphthalene	0.093	0.13	0.10	0.082	0.049	0.080	0.068
biphenyl	0.025	0.063	0.017	0.034	0.024	0.039	0.038
acenaphthene	0.13	0.22	0.19	0.17	0.075	0.14	0.14
fluorene	0.019	0.058	-	0.043	0.021	0.033	0.039
carbazole	0.024	0.043	0.016	0.022	0.010	0.014	0.025
dibenzofuran	0.066	0.079	0.078	0.10	0.078	0.11	0.12
phenanthrene	0.0007	0.0030	0.021	0.031	0.028	0.028	0.041
anthracene	0.0020	0.0090	0.010	0.011	0.0092	0.0080	0.0070

- no data reported for fluorene on sample day 1357

### 3.3 Discussion

It is possible that mainly organics dissolved in the slug of treatment water that passed through the source were oxidized. An attempt was made to relate the mass of permanganate added to the mass of organic compounds present in the dissolved phase to assess the potential of the treatment to have created a low-organic “slug” of groundwater emanating from the treated source. Using the Raoult’s Law model of source dissolution it was estimated that around half a mole of oxidizable compounds would enter the dissolved phase over the 35 day treatment period. The amount of permanganate injected is capable of oxidizing 40 moles of creosote, much more than the half a mole that entered the dissolved phase during this time.

The fact that permanganate was in excess in the injected water was reported by Lamarche (2002) who detected a significant amount of permanganate downgradient of the source (0.3 m monitoring fence). This shows that significant permanganate was available for continued oxidation of dissolved organics in the downgradient plume. Also, retarded organic compounds in the plume overtaken by the permanganate slug could also be oxidized. This slug of deficient organic compounds then migrates at the retarded groundwater velocities and the excess permanganate migrates at groundwater velocity.

The temporary decrease in plume mass for sample day 4315 is consistent with this concept. If the low-concentration treated water is within the monitoring network on post-treatment sampling days the total plume mass of the compound will be reduced. The plume mass of carbazole, 1-methyl naphthalene, acenaphthene, phenanthrene and fluorine is reduced on day 4315 and based on retardation values for each of these compounds the treated slug of water is within the core of the monitoring network. By sample day 5140 the low-concentration volume of water for each of these compounds migrated beyond or to the very edge of the monitoring network where concentrations of these compounds are already minimal. Consequently a rebound in plume mass was observed.

Anthracene is one compound that displays a decrease in plume mass on day 5140 as well as day 4315. Actually the plume mass on day 5140 is less than sample day 4315 for this compound. Anthracene is highly retarded and on sample day 4315 the low

concentration slug of water was only starting to enter the monitoring network. By day 5140 the entire slug of treated water is within the network, explaining the further decrease in mass on this sample day. The slug of excess permanganate would have migrated the full length of the monitoring network prior to the first post-oxidation sampling event (day 4315). Traveling at the velocity of groundwater the excess permanganate would have oxidized retarded organic compounds it over took. There is no evidence for extensive oxidation of retarded compounds such as anthracene in the plume from monitoring on days 4315 and 5140 (see Figure 3.4b).

It is not possible to quantify how much  $\text{KMnO}_4$  migrated through the dissolved plumes, but the impact seems minimal. For example, if 15% of the permanganate injected did not react through the source zone there would be enough  $\text{KMnO}_4$  to oxidize the entire mass of organic compounds in the plume on the last monitoring day prior to the oxidation (day 3619). Because there is no evidence of significant oxidation of organic compounds through the length of the plumes compared to day 3619 (Figure 3.4a,b) it is likely only a minor release of permanganate into the plume occurred.

This concept would be the same for the mass discharge measurements of each compound. If the treated water was in the vicinity of monitoring fence three (location of discharge calculations) at the time of monitoring, the discharge for the compound would be reduced. All oxidizable compounds show some degree of decrease in mass discharge on sample day 4065. On this sample day the retarded but treated compounds were within 2 m of the discharge monitoring fence. Compounds such as carbazole show only a minor decrease in discharge perhaps because only the tail end of the slug of treated water was captured at the monitoring fence. Other compounds such as fluorine, phenanthrene and acenaphthene show a clear decrease in discharge on day 4065 before rebounding to pre-treatment discharge trends on day 4315. Basic retardation calculations show the slug of treated water was around 3 m from the source on day 4065 which is the location of monitoring fence three.

The most notable compound is anthracene. Post-treatment anthracene mass discharge continued to decrease. Anthracene is a highly retarded compound and on day 4065, 4315 and 5140 the treated anthracene slug would have traveled around 2, 3 and 6.5

m from the source zone. The mass discharge monitoring fence is ~3 m from the source, thus the reduced mass discharge in anthracene may be the result of this treated slug of water occupying the area around the discharge monitoring fence. With any future sampling events the slug of treated water will have migrated far enough downgradient that the mass discharge of anthracene should have rebounded as well.

The non-oxidizable compounds, biphenyl and dibenzofuran show no post-treatment change in plume mass. If the source NAPL was significantly effected it would be expected that biphenyl and dibenzofuran plume mass may increase because of enhanced dissolution of the compounds due to removal (oxidation) of more soluble compounds (enhanced mole fractions), this was not observed. Rather Lamarche (2002) observed a slight 15% reduction in mass discharge for both biphenyl and dibenzofuran during the AMD test and the mass discharge of these compounds may have shown a slight decrease on sample day 4065. The observed decrease in discharge on day 4065 for these compounds is within the uncertainty of the mass discharge estimates however.

The calculated mass discharge of each compound was compared to the mass discharge predicted from the Raoult's Law model of source dissolution. For all compounds except anthracene and dibenzofuran the measured mass discharge followed the predicted trend of mass discharge (Figure 3.3) for both pre- and post-oxidation.

Prior to the ISCO, anthracene mass discharge was clearly increasing, as predicted by the Raoult's Law model (Figure 3.3b). Post-oxidation there is a clear and continuing decrease in the measured mass discharge, contrary to the prediction from Raoult's Law. As discussed previously anthracene is highly retarded and it is likely that the oxidized slug of anthracene was still within the area of the mass discharge monitoring fence, causing the low estimate. It is expected that as this slug of water migrates beyond the monitoring fence that the mass discharge of anthracene will rebound.

Up until sample day 1357 the measured mass discharge of dibenzofuran was relatively consistent, as predicted (Figure 3.3d). On sample day 3619, still pre-treatment, mass discharge remained relatively unchanged. According to the model discharge of dibenzofuran into the plume by day 3619 should have been noticeable lower. Post-

oxidation dibenzofuran mass discharge remains constant. Clearly, the measured mass discharge of dibenzofuran does not follow the predicted trend for day 3619 to 5140. This does not necessarily reflect just an effect of the oxidation as the measured mass discharge deviated from the predicted trend prior to the oxidation.

## Chapter 4

### Conclusions

Raoult's Law adequately predicted the dissolution of nine of the eleven compounds from an emplaced coal tar creosote residual source. In general it overestimated mass flux emanating from the source because considerable mass biotransformation was occurring in the source zone.

More than 90% of each monitored compounds (carbazole and biphenyl excepted at 83 and 88%) entering the plume was not accounted for within this 14 year study. For less soluble chemicals the bulk of the mass removal apparently occurred in the source zone. However, the greatest mass loss is in the plume, especially for mobile compounds having high solubility and low partitioning coefficients such as xylenes, phenols and naphthalene.

Oxygen is the major electron acceptor at the site yet the amount of organic compounds unaccounted for cannot be matched through aerobic mineralization or even through partial mineralization alone. In addition, possible partial mineralization products such as organic acids which were detected earlier were not persisting in 2006. Previously detected toxicity agent(s) within the dissolved oxygen shadow in front of the chemical plumes where no creosote compounds are detected were no longer present in the 2006 sampling round. Sorption well in excess of short-term equilibrium estimates may account for at least part of this discrepancy.

Natural attenuation played a dominant role in limiting the extent of dissolved chemicals leached from the source. Groundwater traveled more than 500 m and the contaminants less than 50 m. It is believed in the future that biodegradation will become a more significant control for the other degradable compounds (carbazole, 1-methyl naphthalene) as the naphthalene plume continues to attenuate. Other compound plumes (dibenzofuran and phenanthrene) may continue to expand due to increasing fluxes from the source and apparently limited degradation potential. While the extent of natural attenuation in this study is impressive, the detailed understanding of the controls on the rate of bioattenuation, especially due to interactions between organic substrates, and the

effects of non-equilibrium sorption is not yet demonstrated. This emphasizes the likely need to maintain some monitoring if natural attenuation is employed for such chemically complex sources and plumes.

Laboratory experiments demonstrated that eight of ten compounds of interest were readily oxidized by  $\text{KMnO}_4$ . Biphenyl and dibenzofuran were not reactive. The amount of permanganate injected transformed at most 11% of the source coal tar creosote residual NAPL. This was sufficient to produce a short-term decrease in discharge of organic compounds shown to be reactive with permanganate. In the longer term, reduction of discharge and plume mass was similar or less than the relative error associated with mass discharge and total plume mass estimates, even at this highly monitored site.

Similar mass distribution of the compounds for day 4315 and 5140 make it difficult to determine if the observed decrease in mass within the plume on day 4315 (day 5140 for anthracene) was an effect of the oxidation or the result of changes in sampling density within the high concentration core of the plume.

Over the long term mass discharge of nine of the eleven compounds followed the predicted trend generated by the Raoult's Law model in spite of the ISCO. Anthracene is the only compound that deviated from the predicted mass discharge trend post-oxidation. This is likely the result of the high retardation of anthracene so that the treated "slug" of anthracene was being monitored at the discharge monitoring fence over both sample days.

There was no significant decrease in plume mass or mass discharge for non-oxidizable compounds. For oxidizable compounds once the treated water migrated beyond the monitoring network the mass discharge and plume mass of these compounds returned to pre-treatment trends. The conclusion follows that the *in situ* chemical oxidation of the source zone did not significantly alter the chemical composition of the residual NAPL but rather oxidized mainly the dissolved organics in the source zone. This is consistent with the short term observations by Lamarche (2002), who detected a greater proportion of the permanganate at a downgradient monitoring fence, indicating a significant amount of permanganate did not react in transit through the source zone.



Overall the partial *in situ* chemical oxidation of the coal tar creosote source produced no long term effect on the dissolved plumes emanating from the source. Laboratory testing demonstrated the ability of  $\text{KMnO}_4$  to significantly reduce mass for many target chemicals within a residual NAPL by enhancing mass transfer rates. However, the field application of permanganate sufficient to oxidize only about 10% of the residual source had minimal benefit in reducing the discharge into the plume and the plume extent.

## **Chapter 5**

### **Recommendations**

Following are some general recommendations for additional research related to this work:

1. In depth study to examine transformation products and organic acids that may be at the site. This could be conducted through laboratory testing complimented by plume sampling and may provide insight into the biotransformation processes that are occurring.
2. A clearer attribution of mass unaccounted for to biotransformation or to higher-than-predicted sorption should be made by better defining the sorbed mass in the field. Evaluate the actual concentrations of target organics sorbed onto aquifer material and compare to the prediction based on nearby dissolved concentrations and short-term equilibrium experiments of King et al. (1999). This would provide a better understanding as to what fraction of the mass unaccounted for was biotransformed.
3. To complete the mass balance by excavating and quantifying the remaining source NAPL. This would provide a confirmation of the mass balance of organics and the accuracy of the Raoult's Law model of source dissolution.
4. Conduct sampling of monitoring fence 3 to determine if the discharge of anthracene from the source zone rebounded. This would confirm the theory that the oxidation mainly affected the dissolved contaminants.
5. Continued monitoring of the network to determine how the dominant compounds in the plume evolve over time.

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## **Appendix A**

### **Coal Tar Creosote Database**

This appendix is eight PDF files which contain dissolved concentrations of organic and inorganic compounds collected over the course of this 14 year study.

The file names are “Day 278 (King, 1997) Organic Data.pdf”, “Day 626 (King, 1997) Organic Data.pdf”, “Day 1357 (King, 1997) Organic Data”, “Day 3619 (Blaine, 2000) Organic Data”, “Day 4065 (Lamarche, 2002) Organic Data”, “Day 4315 (Fraser, 2005) Organic Data”, “Day 5140 (this study) Organic Data” and “Day 5140 (this study) Inorganic Data”.

If you accessed this thesis from a source other than the University of Waterloo, you may not have access to this file. You may access it by searching for this thesis at <http://uwspace.uwaterloo.ca>.

Files are labeled for the time (days) of each sampling event with the author’s name in brackets as to where the data is reported. For example “Day 1357 (King 1997) Organic Data” would indicate the data was collected on monitoring day 1357 and reported by King. All references can be found in the reference list.



## **Appendix B**

### **Results for All Compounds Studied**

This appendix is four PDF files which contain mass discharge, total plume mass, dissolved mass distribution and contour plots of all compounds analysed in this study.

The file names of these PDF files are “Mass Discharge.pdf”, “Plume Mass.pdf”, “Plume Contour Plots.pdf” and “Dissolved Mass Distribution.pdf”.

If you accessed this thesis from a source other than the University of Waterloo, you may not have access to this file. You may access it by searching for this thesis at <http://uwspace.uwaterloo.ca>.

## **Appendix C**

### **Toxicological Results**

This appendix is three PDF files that contain the toxicological reports for the *Ceriodaphnia dubia* assay conducted by Stantec.

The file names of these PDF files are “N3-1 Report.pdf”, “9-1 Report.pdf” and “30-3 Report.pdf”.

If you accessed this thesis from a source other than the University of Waterloo, you may not have access to this file. You may access it by searching for this thesis at <http://uwspace.uwaterloo.ca>.

These files are labeled by sample location where “N3-1 Report.pdf” is the sample collected from background, “9-1 Report.pdf” is the sample collected from within the dissolved plume and “30-3 Report.pdf” is the sample collected from in front of the dissolved plume but within the depleted oxygen shadow.