

Temporal Evolution of a NAPL Source Zone Up-gradient of a Pump & Treat System in a Fractured Sandstone Aquifer

Brian K. Ndirangu^{a*}, Beth L. Parker^b, Jessica R. Meyer^{b,c}, Maria Teresa Condesso de Melo^a

^aInstituto Superior Tecnico, Universidade de Lisboa, Av. Rovisco Pais 1, 1049-001, Lisboa, Portugal.

^bG³⁶⁰ Institute for Groundwater Research, University of Guelph, 50, Stone Road E., ON, Canada.

^cUniversity of Iowa, Iowa City, IA 52242, U.S.A.

*Corresponding Author: bkdirangu@gmail.com

Abstract

Performance of dense non-aqueous phase liquids (DNAPL) remediation technologies rely on effectively characterizing source zone architectures spatially and temporally. Using a site in south-central Wisconsin, this study utilized high resolution sampling from rocks cored between 2003 and 2017 and mass discharge analysis from downgradient pumping wells to investigate a contaminated fractured rock site. The results showed an 83% mass reduction in rock matrix volatile organic compound (VOC) mass over the eleven years which occurred at a higher rate in the upper bedrock units. Analysis of mole fractions with depth showed a 57% decrease in chlorinated compounds and a corresponding increase in ketones, benzene, toluene, ethylbenzene and xylenes. Within some sections of the profiles, concentrations of groundwater were within an order of magnitude difference with calculated rock matrix pore water concentrations implying back-diffusion processes within the matrix in certain sections which contributed to the observed source declines. Mass discharge from the pumping wells was approximately sixty times higher than the total mass discharge observed at the source zone transect but closely matched the characteristics from the cored holes in the source zone.

Key words – rock core, chlorinated solvents, fractured sedimentary rock, back-diffusion, high resolution sampling.

1. Introduction

The extensive production and improper handling of household and industrial chemicals such as plastics, paints, gasoline products and pesticides has led to widespread contamination of regional aquifers around the world. In the United States, 77,000 such sites have undergone cleanup work and the US EPA projects that approximately 300,000 sites will need to be cleaned up in the next two decades at an estimated cost of \$209 billion. Of the myriad of contaminants present at hazardous waste sites, organic chemicals in the form of dense non-aqueous phase liquids (DNAPLs), including chlorinated solvents, have been ranked as some of the most expensive and challenging to remediate, especially in fractured media. A major stride towards better decision making for the long-term management of contaminated fractured aquifers lies in understanding the behaviour and spatio-temporal evolution of DNAPLs.

The topic of contaminated aquifers is of central importance especially in light of various aspects of global change. The quadrupling of global population in the last century has resulted into an eight-fold increase in water demand; a further 55% population increase projected by 2050 is likely to increase water stress and shortage. The resulting socio-economic pressures have exacerbated anthropogenic contamination of water resources at a time when water scarcity is prevailing. Groundwater is not immune to these changes – aquifers around the world continue to be polluted by sources which are sometimes detected decades after the original contamination. Such widespread contamination, including DNAPLs underscores the importance of identifying, characterizing, remediating and managing groundwater resources more so in the face of climate change.

2. Study Area

2.1. Site Description and Contaminant History

The field site is located in Cottage Grove, a village located approximately 21 km east of Madison, Wisconsin, U.S.A. (**Figure 1**).

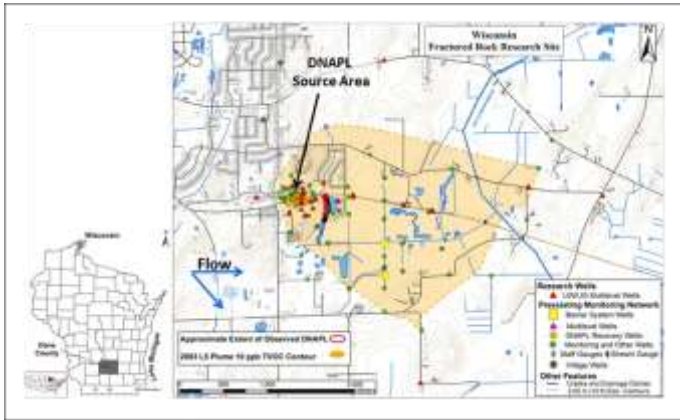


Figure 1 Field location in Dane County, Wisconsin.

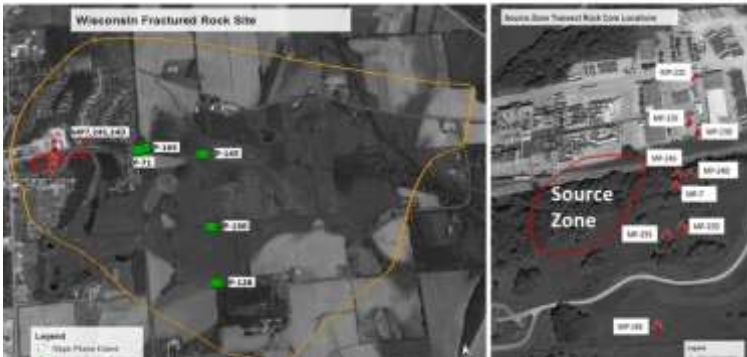


Figure 2 Study area showing the location of the pumping wells and the source zone transect core holes

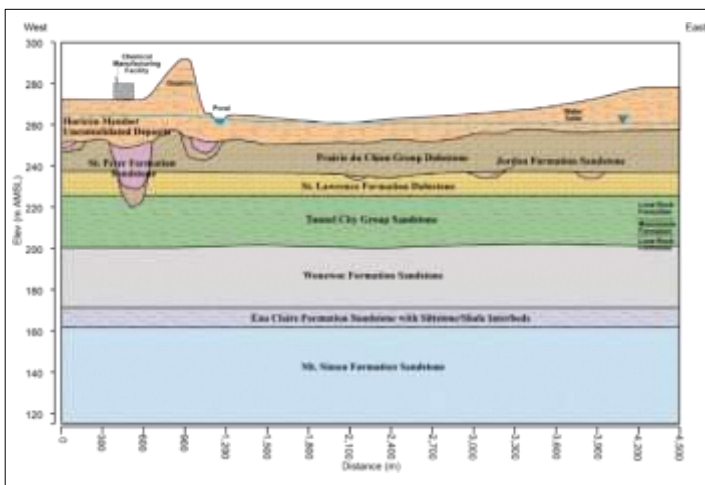


Figure 3 Conceptualization of the site stratigraphy

The field site is characterised by low to moderate topographical relief associated with Pleistocene lacustrine, fluvial, and drumlinised till deposits (Meyer et al., 2016). It encompasses the DNAPL source zone, surrounding wetlands and agricultural land affected by the migrating plume. Data collected from three of the SZT research core holes (MP-7, MP-24S and MP-24D) and 3 pumping wells (P-128, P-130, and P-145) downgradient from the focus of this study with supporting evidence drawn from 6 other cores (MP-22S, MP-23S, MP-23D, MP-25S, MP-25D, MP-26S) within the SZT (**Figure 2**).

2.2. Hydrogeological Conditions

Detailed descriptions of the geology and groundwater flow system at the Hydrite site were presented by Austin (2005) and Meyer (2005); an abridged discussion is presented below and shown in **Figure 3**. The focus of this thesis, the Tunnel City Group, is a permeable Cambrian age siliciclastic rock characterized by fractured sandstone with thin interbeds of siltstone and shale. It consists of two distinct facies that intertongue, namely a glauconitic facies, the Lone Rock Formation, and a non-glaucanite facies, the Mazomanie Formation. Site investigations conducted in the Lone Rock formation by Austin (2005) reported an average porosity of 19%. Meyer (2005) showed that the hydraulic conductivities of the matrix and horizontal fractures differ by four orders of magnitude (1.2×10^{-7} vs 8.6×10^{-3} cm/s) indicating that most of the groundwater flows through the dominant hydraulically active horizontal fractures. Estimates of organic carbon fractions (f_{oc}) reported by Lima et al. (2012) at this study site were below the 0.1% threshold for organic carbon dominated sorption. However, sorption processes differ depending on the solubility of the compounds: low fractions of organic carbon can control sorption of very hydrophobic compounds whereas highly soluble compounds are not sorbed in geologic media with low organic carbon content. Generally, the shallow and deep groundwater systems in Dane County are connected.

2.3. DNAPL Contamination

During site construction activities at a chemical recycling facility in Wisconsin in 1982, the soil, and later groundwater, were found to be contaminated with DNAPLs which had been released into the subsurface prior to 1970 before the property was acquired. Subsequent site characterisation showed that the contaminants migrated through the unconsolidated glacial sediments and into the upper bedrock units, before settling at a depth of between 45 to 56 m below the surface in the upper part of the fractured Tunnel City sandstones

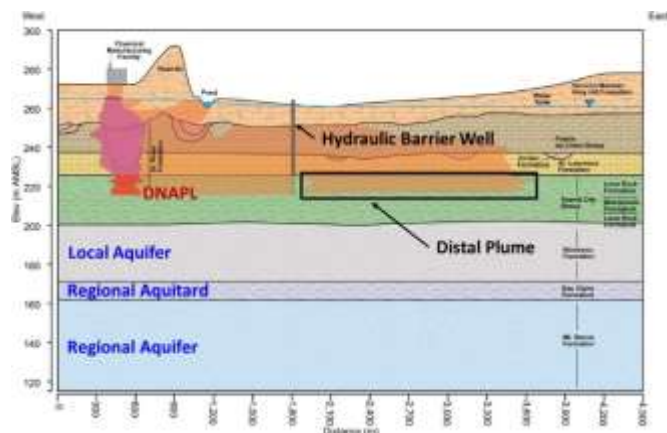


Figure 4: Stratigraphic Cross-Section showing the DNAPL.

(Figure 4). The current location where the DNAPL resides, hereafter called the source zone, is located between 40 and 100m south of the release area. West-East groundwater flow through the source zone has resulted into a dissolved-phase plume that has migrated downgradient and measured 2.8 km long at its maximum lateral extent in 2003. To avoid the plume, the private wells in the plume's path were deepened. Four municipal wells that are cross-gradient with respect to the dissolved phase plume pump water from the deeper Mount Simon formation and have not reported any contamination from this plume. A hydraulic barrier system (HBS) consisting of three pumping wells was installed in 2003 to cut off the plume from the source zone and prevent farther migration down-gradient. Since the discovery of the

contamination, a variety methods have been utilised to recover the DNAPL from the soil and the subsurface, especially the upper Tunnel City sandstones. The remaining volume is believed to be the major DNAPL reservoir at the Hydrite site.

3. Materials and Methods

3.1. Rock Core Sampling

Between 2003 and 2017, eleven research holes were drilled to investigate the vertical distribution of contaminants within the low permeability rock matrix near the source zone. These core holes were drilled along a North-South transect eighty meters downgradient of the source zone and roughly perpendicular to the West-East groundwater flow direction. Figure 2 shows the location of nine SZT research core holes: MP-7 drilled in 2003; five shallow bedrock holes (designated with an 'S') drilled in 2014 (MP-22S, MP-23S, MP-24S, MP-25S and MP-26S); and three deep bedrock holes (designated with a 'D') drilled in 2017 (MP-23D, MP-24D, and MP-25D). Of these core holes, MP-7, MP-24S and MP-24D cored in 2003, 2014, and 2017 respectively are co-located within a nine meter radius. They serve as the central focus of this study by providing a unique opportunity to evaluate temporal changes of the contaminant mass and distribution within the source zone.

3.2. Groundwater Sampling

Depth-discrete multilevel systems (MLSs) are powerful yet cost-effective engineered solutions for complex fractured rock sites because they maximize the quantity of data obtained from a single borehole. The Westbay® System MLS offers the largest number of monitoring zones within the typical borehole dimensions used in this study (Meyer et al., 2014). Westbay Systems®, henceforth termed Westbays were selected to facilitate depth-discrete measurement of hydraulic pressure and collection of groundwater samples at MP-7 in 2005 and MP-24S.

3.3. Hydraulic Barrier System Measurements

Five pumping wells that constitute an HBS were installed in 2003-2004 to cut off the plume from the source zone and prevent further contaminant migration downgradient. These pumping wells are located between 0.5-1.2 km downgradient from the SZT and are screened between 38-48mbgs corresponding to the Tunnel City Group where most of the residual DNAPL lies. As of December 2017, only 3

pumping wells (P-164, P-128, and P-130) were operational and constitute the HBS. Pumping volumes recorded were combined with groundwater concentration data to glean information on mass discharge and the quantity and composition of the extracted VOCs.

4. Results and Discussion

4.1. VOC Concentration in Rock matrix

Results of rock core VOC sampling show that the total contaminant mass per square meter of core declined from 8.78 moles (815.70 g) to 1.89 moles (163.91 g) between MP-7 cored in 2003 and MP-24S cored 2014 and to 1.46 moles (121.54 g) in MP-24D cored in 2017 (**Figure 5**). These declines represent changes of 78.5% between MP-7 and MP-24S and 22.7% between MP-24S and MP-24D. The overall decrease in moles over the fourteen-year period was 83.4% measured with MP-7 results as the baseline. Over this time period, chlorinated methanes and ethenes recorded the highest declines, 99% and 95% respectively, whereas ketones displayed the lowest decline of 42%. The mass of chlorinated ethanes declined by 89% and that of BTEX compounds by 77%.

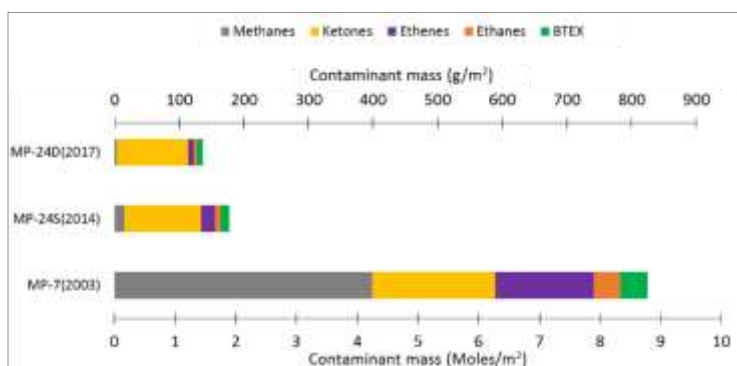


Figure 5 Mole profiles of contaminant groups with depth (moles/m² of rock core).

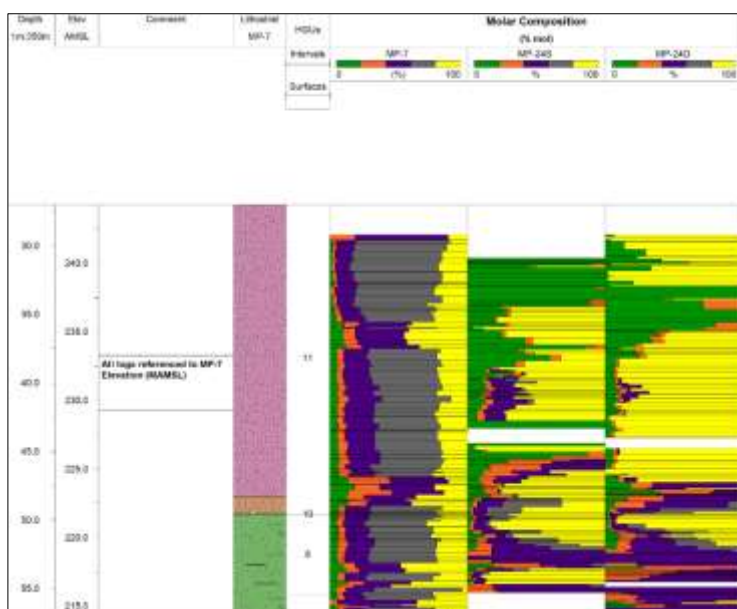


Figure 6 Contaminant groups profiles for each of the three core holes.

longest operating well closest to the source zone has extracted the highest volume of groundwater as well as the highest contaminant mass.

In addition to contaminant mass changes with depth, the relative composition of the five key contaminant groups (as a percentage of TVOC at every ~30cm interval) is shown in **Figure 6** below. MP-7's profile was comparatively consistent with depth: chlorinated methanes, ethenes, and ketones dominated the composition at most depths. The composition changed in MP-24S and MP-24D where ketones and BTEX compounds dominated most of the profile, especially in the upper bedrock units. Within lower units, the percent molar composition of chlorinated ethenes increased significantly whereas the ketones and BTEX composition was generally below 5%.

4.2. Analysis of the Hydraulic Barrier System

Groundwater samples and pumping rates from the HBS were analysed and reported. Between 2003 and 2017, the five pumping wells that originally constituted the HBS pumped out approximately 3225.8 megalitres (ML, x106L) of groundwater and extracted 260 573 moles (23 693 kg) of TVOCs as shown in **Table 1** below. 91.6% of the TVOC mass was extracted between 2003 and 2014 before the SZT cores were collected, with the exception of MP-7 cored in 2003 before the HBS came online. As discussed earlier, two pumping wells, P-71 and P-145, were taken offline in 2004 and 2008. They constitute less than 5% of the groundwater volume pumped out and 13% of the total mass of TVOCs extracted. Consequently, only pumping wells P-164, P-130 and P-128 currently constitute the HBS and therefore were the only ones analysed in detail. P-164 that is the

Table 1: Pumping wells operating conditions.

Well ID	Distance		Sampling Period*		Groundwater pumped (x10 ⁶ L)	TVOC removed (kg)
	from the SZT(m)		Start	End		
P-128	1296		Oct-2003	Dec-2017	805.44	294.08
P-130	1075		Oct-2003	Dec-2017	816.03	851.58
P-145	947		Oct-2003	Sep-2008	119.455	1,134.90
P-164	573		Aug-2004	Dec-2017	1459.193	19,383.94
P-71	541		Mar-2004	Sep-2004	25.669	2,028.67
					3225.78	23,693.17

5. Discussion

5.1. Causes of the Source Zone VOC Declines

Multiple lines of evidence were drawn to gain a deeper understanding on possible mechanisms occurring in the up-gradient source zone and the influence of the HBS on the contaminant changes observed in the SZT core holes: 1) the role of DNAPL composition on the effective solubility of VOCs and the effect on mass persistence patterns; 2) possible zones of back-diffusion processes from the low-permeability matrix into the fractures upon which groundwater transports the contaminants downgradient and 3) the influence of the pumping wells on source zone mass declines. Supporting evidence from previous studies on microbial-mediated natural attenuation mechanisms were also examined as they play a role in degrading contaminants *in situ* within the low permeability matrix to produce different by-products and secretions.

Variations in the Effective Solubility of the Oily-phase NAPL Components

Effective solubility is useful in predicting the dissolution and mass distribution patterns of contaminants under the influence of flowing groundwater. The hypothesis is that contaminants ranked as having very high effective solubility values will dissolve much faster than those with relatively low values which will tend to persist. Effective solubility were calculated using the equation below: $S_e^i = \chi S_w^i$ where (S_e^i) is the effective solubility of a component i in a NAPL mixture, (S_w^i) is the pure-phase solubility of a component i in pure water and χ is the mole fraction. The calculations showed the Dichloromethane, Trichloroethene, 1,1,1-trichloroethane, and Toluene had the highest effective solubilities of the original NAPL compounds.

Back-Diffusion of VOCs from the Rock Matrix into the Fractures

In mature contaminated sites where most of the NAPL phase in the fractures has been dissolved by flowing groundwater, the concentration gradient changes which causes back-diffusion of the contaminants from the matrix to the fractures. To investigate whether back-diffusion could have contributed to the observed rock core contaminant mass declines, concentration of groundwater sampled from the fractures in the core holes (C_{gw}) was compared to the hypothetical pore water concentration (C_{pw}) - the concentration of aqueous-phase contaminants in the rock matrix that would be in equilibrium with the groundwater in the adjacent fractures. This pore water concentration can be expressed as: $C_{pw} \left(\frac{mol}{L} \right) = C_t \left(\frac{mol}{g_{wet\ rock}} \right) \frac{\rho_{wb} \left(\frac{g_{wet\ rock}}{L} \right)}{R \times \theta_m}$ where (C_t) is total concentration of the wet rock core, (ρ_{wb}) the wet-bulk density, (θ_m) the interconnected matrix porosity and (R) the retardation factor. If $C_{pw} \geq C_{gw}$, the concentration gradient may act as a driving force for back-diffusion mass transfer from the matrix to the fractures thereby suggesting a potential mechanism

for the observed rock core mass loss. However, unless big discrepancies are noted, it cannot be said with confidence whether pore water concentrations are greater than groundwater concentrations

Figure 7 below shows that the groundwater concentrations are generally higher than the rock core pore water concentrations by 0.5-1 order of magnitude. In general, higher VOC concentrations in fracture groundwater compared to adjacent rock matrix pore water is

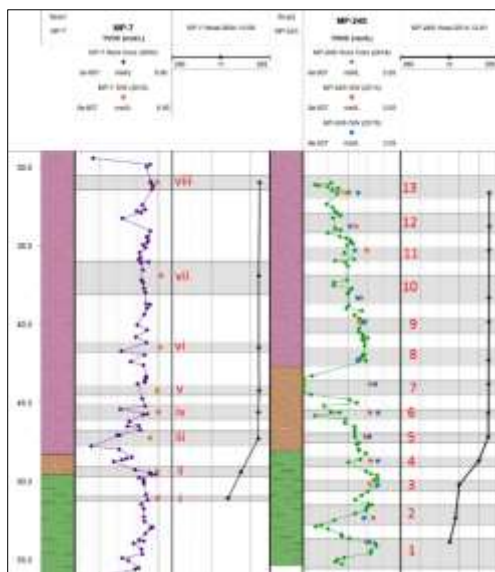


Figure 7 Comparison of groundwater and equivalent pore water concentrations

meant to serve as one line of evidence for the possibility of back-diffusion. However, significantly high groundwater concentrations could represent upgradient sources of origin rather than represent groundwater adjacent to the rock matrix or because the downgradient pumping wells are inducing groundwater flushing from the source zone where concentration of contaminants is highest. In summary, this comparison is very useful in understanding back-diffusion sources but other competing mechanisms should be appreciated and examined in order to make sure that the right conclusions are drawn.

Possible Causes of Mass Changes in Individual Contaminants

Changes within each of the five contaminant groups were analysed to understand feasible process contributing to the observed source-zone declines. The contaminant groups ranked in descending order based on the observed source zone declines of that group across time are: chlorinated methanes (99%), chlorinated ethenes (95%), chlorinated ethanes (89%), BTEX (77%) and ketones (42%).

Chlorinated methanes declined by 99% between MP-7 and MP-24D - the highest overall decline among the five contaminant groups. A hypothesis is that most of the chlorinated methanes from the source zone could have been dissolved and transported into the down-gradient plume or degraded by autochthonous bacterial communities or a combination of both. The increased rate of groundwater flushing may have increased the concentration gradient between the matrix and the fractures, enhancing the mass decline observed at the core holes

Chlorinated ethenes recorded an overall decline of 95% between MP-7 and MP-24D. These compounds were dissolved by flowing groundwater and transported to down-gradient locations where they eventually diffused into low permeability matrix. Active solvent-tolerant microbes that thrive in the matrix degraded PCE and TCE, transforming them into cis-DCE, a daughter product of anaerobic reductive dechlorination. The concentration of PCE and TCE between 2003 and 2017 reduced to non-detect in most sections of the profile, showing evidence of microbial action.

The main chlorinated ethane in the original NAPL was TCA which constituted 38 and 26% of the mole fraction of the original DNAPL. The effective solubility of TCA was amongst the highest in the original NAPL which may have led to faster dissolution and transport down-gradient and through molecular diffusion, it accumulated in the low-permeability matrix where it further underwent microbial degradation.

BTEX compounds are very persistent owing to their high sorptive capacity and very low solubility, relative to other VOCs. Of the BTEX compounds, toluene had the highest presence in the original NAPL which could explain its high presence in MP-7. Toluene also recorded the fastest declines within the BTEX group compared to MP-24S and MP-24D samples. This could be because toluene acted as an electron donor (reductant) in the anaerobic reductive dechlorination of TCE, cis-DCE and VC in groundwater (McCarty et al., 1998).

Tests conducted at RW-58 and RW-111 did not show any ketones present in the NAPL. However, at all three core holes, MEK and MIBK are not only present but they account for 80% of the TVOC at MP-24D core hole. Microbial communities may have used toluene as an electron donor to dechlorinate TCE, cis-DCE and VC can convert some of the organic matter in the aquifer to MEK. Fowler et al.

(2011) elucidated this possibility by examining four sites under active remediation where acetone and MEK were noted to increase in the groundwater. One of the main conclusions of the study was that some microbial communities secrete acetone and MEK as metabolic intermediates especially in the absence of methanogenic conditions. However, very scarce research has been published on ketones in contaminated aquifers and the corresponding microbes that secrete them. The second possibility for the increase in the mass of MEK is that there may be another source zone nearby whose spill contained copious amounts of MEK. This theory is feasible given that the exact NAPL spill components, locations and times are not well documented or understood. If another source zone exists, it could be responsible for the ketones observed at MP-24S and MP-24D.

5.2. Comparison of the Source Zone to the Downgradient Pumping Wells

The second key research objective was to investigate how the mass and composition changes within the source zone compare to that captured by downgradient pumping wells. To answer this question, source function (defined by source zone mass discharge) and mass discharge comparisons have been identified from literature as a good candidate for this evaluation (SERDP & ESTCP, 2006) and have been applied at various source and plume scales (e.g Einarson & Mackay, 2001; Guilbeault et al., 2005; C J Newell et al., 2003). The transect method was used to estimate the mass discharge across the SZT using a similar approach to those suggested by Guilbeault et al. (2005) and Ricker (2008). The first step involved analyzing the plume concentrations with depth across the SZT and interpolating the concentration data in between the core holes. The second step involved characterisation of groundwater flow to obtain the horizontal bulk hydraulic conductivity, K_h , and hydraulic gradient, i , which would enable calculation of the average Darcy flux (q) and volume discharged through each hydrogeological or geologic unit of the source zone. The third and final step involved identifying and calculating the 2-D plane of the SZT whose area contributes to mass discharge. The cumulative mass discharge across the SZT was calculated according to the method listed in ITRC (2010) modified as shown below: $M_f = \sum_{j=1}^n C_j K_{h,j} i_j A_j CF$ where M_f is the cumulative mass discharge in g/s, j is the grid number in the SZT, C_j is the concentration in g/L, $K_{h,j}$ is the horizontal bulk hydraulic conductivity

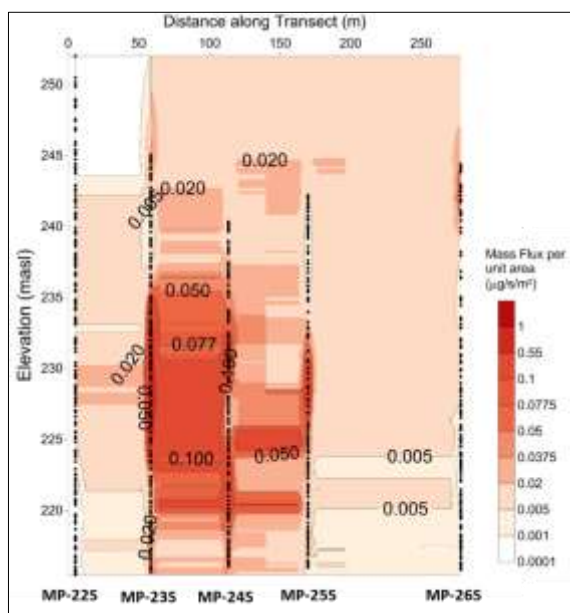


Figure 8 Interpolated mass discharge across the SZT.

of grid j in cm/s, i is the hydraulic gradient, A is the area of the grid in cm^2 and CF the conversion factor of 10^{-3} L/cm^3 . Upon interpolating across the entire SZT, the total mass discharge was found to be between 332.8 and 997.4 $\mu\text{g/s}$ (**Figure 8**). These values are within an order of magnitude difference which is acceptable given that parameters of hydraulic conductivity and concentration vary by more than two or three orders of magnitude over short intervals. This value was assumed to represent the mass discharge in 2014 when the “S” boreholes were cored. The calculated mass discharge from the source zone was used to estimate the maximum concentration of the pumping wells using the approach discussed by Einarson & Mackay (2001) and presented in the equation $C = \frac{M_d}{Q_{avg}}$ where M_d is the mass discharge in g/s, C is the concentration of the contaminants sampled from the wells in g/L and Q_{avg} is the monthly average pumping rate in L/s. The observed TVOC concentrations sampled from the wells was combined with the monthly average pumping rates to obtain the mass discharge from the pumping wells. This value was then compared to that from the source zone.

The groundwater samples from the pumping wells were collected every quarter, except in a few instances where sampling did not take place. Given that the pumping schedule was frequently interrupted and the pumping durations irregularly monitored, the monthly average pumping rate was seen as a better representative value than daily pumping rates. A comparison between the source zone and

pumping wells mass discharge is shown in **Figure 9**. Comparing the mass discharge from the source zone with the mass discharge from the pumping wells shows that the pumping wells draw contaminants at a rate that is 59.8 times faster than the rate of mass loss from the

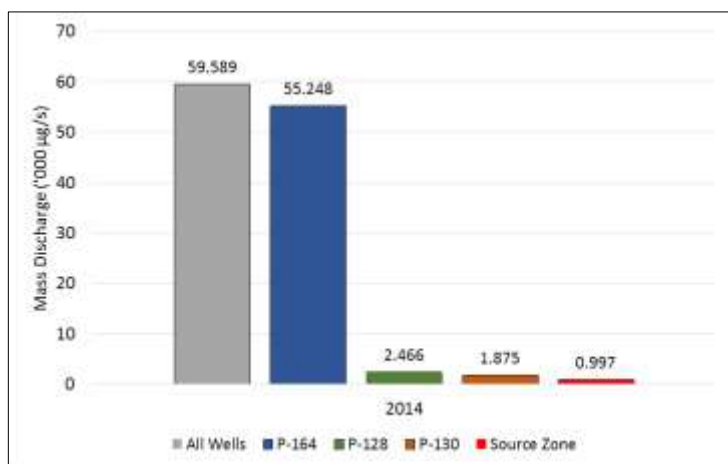


Figure 9 A comparison of the source zone mass discharge with the barrier system mass discharge.

However, the calculated discharge for 2014 may not significantly change given that most of the mass loss in 2014 occurred in the upper bedrock. The second reason relates to natural source zone depletion. Given the evidence for microbial-mediated attenuation in the source zone, the mass from the source zone may not all be flowing downgradient to the pumping wells. The rate of natural attenuation can be estimated and deducted from this mass discharge to isolate the fraction that is flushed down-gradient and captured by the barrier system

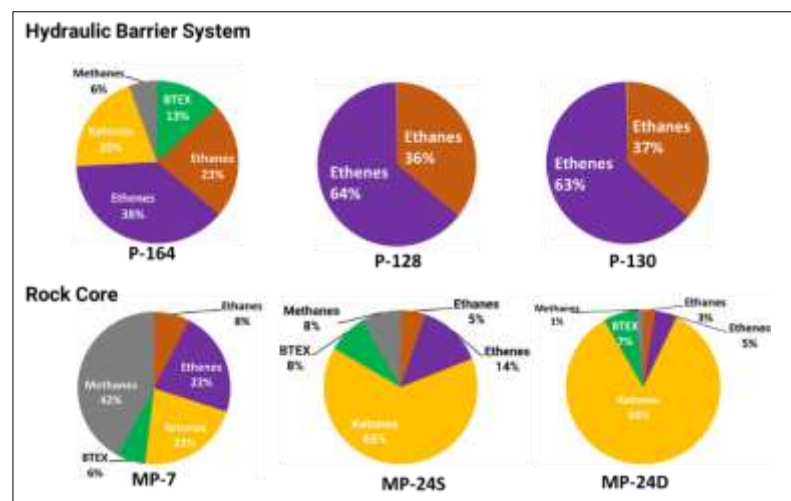


Figure 10 Source zone and barrier system contaminant composition.

well. Another limitation is that the mass captured by the barrier system may originate from other sections of the plume created from the contaminant mass between 1970 and 2003. This could explain the relatively high mass captured by the barrier system in comparison to the mass discharge originating from the source zone. This last limitation is examined in finer details below.

Understanding the sources of contaminant mass captured by the pumping wells is crucial to qualifying the large difference in mass discharge. The composition of the contaminants from the source zone was compared to the composition of the contaminants extracted from the pumping wells. The results are summarised in **Figure 10**. The composition of the source zone core holes contained varying percentages of the five key contaminant groups used in this study. Of the three pumping wells, P-164's composition closely resembled that observed from the source zone core holes. P-128 and P-130 were composed primarily of chlorinated ethenes and ethanes. Several hypotheses can be used to suggest mechanisms to explain the composition differences and similarities. The composition of the sampled NAPL showed that it was majorly composed of chlorinated ethanes and ethenes (TCA, TCE and PCE). Groundwater flow in the last four decades dissolved these three contaminants from the source zone and transported them downgradient, creating a plume. Biodegradation of these compounds to lower molecular weight chlorinated ethanes and ethenes occurred both in the rock matrix and along the groundwater flow path. When the pumping wells began operating in 2003, most of the mass captured was most likely from

source zone, according to the 2014 comparison. This comparison is not sensitive to the year of comparison with the barrier system i.e. comparing the source zone mass discharge with 2014-2017 results does not yield any significant changes. Therefore, these values are comparable without taking into account the time lag between the source zone and the downgradient barrier system.

The above comparison between the source zone and pumping wells comes with a number of caveats. The first is that the core holes that make up the SZT are only cored in the shallow bedrock that consists of the Prairie du Chien (Tonti and Readstown) and St. Lawrence formations. It is likely that the mass discharge calculated is underestimated because it does not include rock core VOC data from some sections of the lower Tunnel City Group, which could potentially increase the total mass discharge.

the plume. The composition of P-128 and P-130 support this hypothesis. P-164 is closer to the source zone than the other two wells and therefore likely captures mass from both the plume and the source zone.

Two lines of evidence have been presented to compare the source zone and downgradient wells: mass discharge and composition analysis. The first showed that the mass discharge emanating from the source zone is over one order of magnitude lower than the total mass discharge captured by the barrier wells. The second showed that the composition of two of the three pumping wells is more indicative of the plume characteristics than the source zone composition. However, refining each of these analysis is required to quantify exactly how much of the source zone mass loss is influenced by the downgradient barrier wells.

6 Summary and Conclusion

6.1 Temporal Contaminant Mass Variation

The results presented showed a significant decline in the rock matrix contaminant mass along the SZT over the fourteen year analysis period. Contaminant concentration trends within the rock matrix varied depending on the position in each core hole as well as with time when the three core holes were examined. In addition to mass, the composition of contaminants varied temporally and also with depth.

Two key groupings were done which enabled key trends to be identified, quantified and discussed. The first grouping was performed by examining cumulative mass curves within each profile and identifying zones based on the mass distribution. Four key zones were identified: two with a high rate of mass loss and two where the mass distribution was lower. A previous analysis showed that majority of the contaminant mass loss occurred in the upper bedrock. This study has refined this mass loss characterisation by showing that between 2014 and 2017, most of the mass loss occurred from the lower bedrock. A key reason for this shift was that after 2014, most of the contaminants in the upper bedrock had already declined to non-detect concentration and thus there was very little mass available to decline in subsequent years. This result implies that the sections of mass loss within the source zones vary with time. Learning more about this variation may be useful when designing depth-targeted remediation systems. Such systems could target zones that are persistent, leaving those where the rate of mass loss is high. On the other hand, delineating sections of the source zone that contribute the highest mass to downgradient plumes can aid in effective plume management strategies.

The second grouping that was done to better understand trends was based on contaminant mass. A closer examination of the contaminant mass at MP-7, MP-24S and MP-24D showed that only 15 of the 35 VOCs that were reported by the laboratory contribute to 99.99% of the total contaminant mass. 13 of these compounds registered mass declines while three displayed an overall mass increase. The declining compounds were primarily higher molecular weight chlorinated compounds as well as compounds whose effective solubilities were relatively high. Each of the three contaminants whose mass increased could have been as a result of different processes within the source zone. Evidence was drawn from previous studies on microbial communities in the rock matrix, geological and hydrogeological characteristics such as erosional unconformities in the upper bedrock, physical parameters such as organic carbon estimations, hydraulic conductivities of the fractures versus matrix and vertical head gradients to understand possible reasons for mass decline, accumulation or persistence. All these contributing mechanisms require closer examination to understand which, if any, are dominant and which ones govern contaminant patterns.

6.2 Evaluating the Efficiency of the Hydraulic Barrier and its Effect on Source Zone Changes

The mass discharge from three down-gradient pumping wells was quantified using quarterly contaminant concentrations and monthly averaged pumping rates. The three wells each experienced a statistically significant step trend in pumping rates, which had an effect on mass discharge patterns. The mass discharge from the source zone was estimated using two interpolation methods which yielded values within the same order of magnitude. On comparing the two, mass discharge from the pumping wells was sixty times higher than the mass discharge calculated for the source zone. This discrepancy was attributed to the pumping wells capturing mass from the distal plume that was created from the time the original spill occurred. Given that the size of the plume has decreased since 2003 when it was at its maximum spatial extent, it is likely that the mass captured by the barrier wells has a large contribution from the

plume. However, given that one of the wells, P-164, has a similar composition that closely matches that from source zone core analysis, a fraction of the source zone mass decline can be attributed to the pumping wells.

7 Recommendations

Several salient aspects of this research would benefit greatly from further studies. Understanding the reasons behind the variable source zone degradation rates with depth will be a valuable step towards characterising sources of mass loss. Chappelle et al. (2012) estimated a biodegradation rate using contaminant concentrations, effective porosity measurements, estimation of chloride concentrations and groundwater residence time. This simple estimate can be used to provide degradation rates that can be then refined using data such as CSIA results and other chemical data. This quantification is important because it serves as a starting point to assess the contribution of natural source zone depletion to the total declines observed in the source zone. The four zones that have been delineated based on mass distribution patterns would benefit from correlations with visible features such as fracture intensity and aperture, lithological changes and heterogeneity, and inorganic constituents in groundwater. Identifying these zones would enrich the understanding on zones of mass loss and how they contribute to mass discharge. The analysis of the mass discharge shows that it may vary considerably over time. A key research question would be to investigate the influence of depth on mass loss and investigate the physical and redox conditions changes with depth and correlate these changes to the survival of certain microbial communities.

Finally, the mass discharge from the pumping wells can be better quantified using an analytical solution such as the integral pumping test approach. However, available analytical solutions should be modified to account for the hydrogeological heterogeneity which influences the capture zone of the wells. Bayer-Raich et al. (2003) develop a particle tracking tool for highly heterogeneous aquifers. A similar approach is required for this site as opposed to more common analytical methods that assume a homogenous aquifer. The capture zone can then be estimated to determine the likelihood of the pumping wells capturing mass from geological units above and below the screened unit. Such a result would be beneficial in informing site managers and environmental regulators on how pump and treat systems alter the contaminant mass and composition in the plume and on the effect of pumping on the source zone.

8. Acknowledgements

I would like to thank my supervisors: Dr. Teresa Melo, Prof. Beth Parker and Prof. Jesi Meyer for engaging me in a very unique and challenging field of research and equipping me with valuable skills that will continue to serve me beyond this research period. I would also like to thank the GroundwatCH coordinators from The Netherlands, Portugal and Germany, Tibor Stigter, Luís Ribeiro and Christian Bernhofer for their thoughtful input in creating such an exciting program and for the Erasmus Mundus funding opportunity. This thesis was developed in CERIS - CIVIL ENGINEERING RESEARCH AND INNOVATION FOR SUSTAINABILITY, a research center of Instituto Superior Técnico of Lisbon in the context of the R&D activities of the group Hydrogeology and Geosystems.

9 Selected References

- Austin, D. C. (2005). Hydrogeologic Controls on Contaminant Distribution Within a Multi- Component DNAPL Zone in a Sedimentary Rock Aquifer in South Central Wisconsin. University of Waterloo.
- Basu, N. B., Rao, P. S. C., Falta, R. W., Annable, M. D., Jawitz, J. W., & Hatfield, K. (2008). Temporal evolution of DNAPL source and contaminant flux distribution: Impacts of source mass depletion. *Journal of Contaminant Hydrology*, 95(3–4), 93–109.
- Brusseau, M. L., Nelson, N. T., Zhang, Z., Blue, J. E., Rohrer, J., & Allen, T. (2007). Source-zone characterization of a chlorinated-solvent contaminated Superfund site in Tucson, AZ. *Journal of Contaminant Hydrology*.
- Buckley, A. (2017). Contaminant Mass Distribution of a Mixed Organic Contaminant Plume Down-Gradient of an Aged DNAPL Source Zone in Sedimentary Rock. University of Guelph. Retrieved from <http://hdl.handle.net/10214/10464>
- Meyer, J. R. (2005). Migration of a Mixed Organic Contaminant Plume in a Multilayer Sedimentary Rock Aquifer System. University of Waterloo (M.Sc. Thesis).
- Parker, B., Cherry, J., & Chapman, S. (2012). Discrete Fracture Network Approach for Studying Contamination in Fractured Rock. *AQUAMundi: Journal of Water Science*, 3(2), 101–116. <https://doi.org/10.4409/Am-052-12-0046>
- Parker, B. L., Chapman, S. W., Goldstein, K. J., & Cherry, J. A. (2018). Multiple lines of field evidence to inform fracture network connectivity at a shale site contaminated with dense non-aqueous phase liquids. Geological Society, London, Special Publications, 479, SP479-8.