Investigation of Pharmaceutical Compounds in Landfill and Septic System Plumes

by

Kelly Stafford

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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

Two municipal landfills and one public septic system in Southern Ontario were studied as potential sources of the pharmaceuticals ibuprofen, carbamazepine, gemfibrozil, caffeine, sulfamethoxazole, and naproxen to groundwater. The background chemistry at each site was also determined. Pharmaceutical analysis was conducted using isotope dilution techniques, coupled with solid phase extraction followed by high performance liquid chromatography electrospray tandem mass spectrometry (HPLC-ESI- MS/MS). An assessment of method performance and extensive quality assurance and quality control practices were employed. At the septic system site, pharmaceuticals were detected at the furthest sampling point, 30 m downgradient from the source area. The highest concentrations measured in groundwater were for carbamazepine (2,050 ng L^{-1}), sulfamethoxazole (1,990 ng L^{-1}) and ibuprofen (1,790 ng L^{-1}). The other pharmaceuticals analysed were observed at concentrations in the range of <1 to 10 ng L^{-1} (gemfibrozil), <8 to 625 ng L^{-1} (naproxen), and <1 to 160 ng L^{-1} (caffeine). Under saturated groundwater transport, attenuation was not strong within the plume as all pharmaceuticals were detected at distance from the source. In the unsaturated zone, most pharmaceuticals appeared to be more greatly attenuated than in the saturated zone. This greater extent of removal in the unsaturated zone is attributed to increased degradation associated with elevated oxygen concentrations. At the two landfill sites, no pharmaceutical compounds were detected in any of the groundwater samples collected within previously defined plumes. Assuming these drugs are disposed in landfill wastes, the absence of detections suggests degradation and attenuation of these pharmaceuticals is occurring. Some of the conditions that may contribute to attenuation include a thick unsaturated zone, strongly reducing conditions, and high sorptive capacity of the waste. Specifically, waste typically

has a higher organic content than aquifer materials, and a lower pH, particularly in the early stages of decomposition. These conditions would result in a potentially higher attenuation of drugs within the waste pile. This study suggests that management programs focused on protection of groundwater quality should take into consideration the potential persistence of pharmaceuticals in septic system environments.

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1.0 Introduction

1.1 Pharmaceuticals in the Environment

Pharmaceutically active compounds (PhACs) are gaining increased attention in the literature and media alike. There are a variety of reasons for this increased attention, including the unknown impact of PhACs to both human and ecosystem health, and the potential additive effects of PhAC exposure. Whereas each pharmaceutical is typically found at a low concentration, the combination of multiple PhACs can result in environmentally significant concentrations. With improved analytical methods capable of detecting PhACs in environmental samples, often with complex matrices, it is possible to study the fate and transport of PhACs at ever decreasing concentrations. In this study, the pharmaceuticals of interest are carbamazepine, caffeine, ibuprofen, sulfamethoxazole, naproxen and gemfibrozil.

Studies have documented the presence of many pharmaceutical compounds, including those of interest in this study, in sewage effluent, surface waters and groundwater. Sources of PhACs to surface water and groundwater can include sewage effluent, runoff from agricultural applications, waste disposal sites, septic systems, and pharmaceutical production plants (Figure 1.1). An extensive review of surface waters in the United States indicated that 62 % of the rivers evaluated were observed to have at least one of the 22 pharmaceuticals measured (Cahill et al., 2004), with caffeine and triclosan being two of the most frequently detected (Kolpin et al., 2002). Caffeine was detected in approximately 60% of the rivers sampled, with a maximum concentration of 6 $\mu g\ L^{-1}$ (Kolpin et al., 2002). Ibuprofen (1.0 $\mu g\ L^{-1}$), gemfibrozil (0.79 $\mu g\ L^{-1}$) and sulfamethoxazole (1.9 $\mu g\ L^{-1}$) were also detected (Kolpin et al., 2002). Extensive reviews of existing literature on the presence of pharmaceuticals in

the environment also have been completed (Halling-Sørensen et al., 1998; Heberer, 2002; Nikolaou et al., 2007; Khetan and Collins, 2007), illustrating the number of studies on this subject and the increasing detection of PhACs in environmental samples.

Sewage effluent has been identified as a major source of pharmaceuticals to surface water (Heberer, 2002; Vieno et al., 2006; Yu et al., 2006; Gros et al., 2007; Nikolaou et al., 2007). The pharmaceuticals that were a part of this study have been detected in surface waters as a result of sewage effluent. Yu et al. (2006), found the presence of ibuprofen (250 ng L^{-1}), naproxen (380 ng L^{-1}) and gemfibrozil (130 ng L^{-1}) in treated sewage effluent discharging to surface waters. Vieno et al. (2006) observed sewage effluent with carbamazepine concentrations up to 470 ng L^{-1}, with recipient surface waters having a maximum concentration of 66 ng L^{-1}. In one study, caffeine was detected at concentrations ranging from 13 to 107 ng L^{-1} downstream of a sewage treatment plant (Rabiet et al., 2006). A survey in Spain investigating concentrations of river systems downstream of sewage treatment plants identified multiple drugs, including caffeine (305 ng L^{-1}), ibuprofen (44 ng L^{-1}), naproxen (9 ng L^{-1}), gemfibrozil (2.3 ng L^{-1}) and carbamazepine (56 ng L^{-1}) (Pedrouzo et al., 2007). Additional studies have identified agricultural runoff as a source of PhACs to surface waters (Lissemore et al., 2006). More recently, attention has been directed towards the investigation of PhACs in groundwater, which is the focus of Chapters 2 and 3.

1.2 Introduction to Study

The six drugs included in this investigation, carbamazepine, sulfamethoxazole, caffeine, naproxen, gemfibrozil and ibuprofen, were selected based on their high prescription rates,

presence in other environmental settings, and in some cases, their observed persistence in the environment. Carbamazepine, for example, is considered an environmentally relevant PhAC because it is fairly recalcitrant, and has been identified in previous literature as an indicator for urban influence on water systems primarily because it is consistently detected in surface water and groundwater, it is fairly conservative, but still capable of disrupting aquatic environments (Strauch et al., 2008). The drugs selected for this study cover a wide range of properties such as solubility, medicinal use, acid-base dissociation constant (pK_a), and octanol-water partitioning coefficient (K_{ow}), which allows for a broad range of interpretation of transport properties in a variety of settings.

The settings investigated include groundwater flow systems downgradient of two municipal landfills and one septic system. The two municipal landfills are both engineered landfills, where one closed recently and is no longer accepting waste. The second is still operating. Both sites are characterized as having a thick vadose zone above the water table, with well-defined groundwater plumes containing organic and inorganic contaminants (Region of Waterloo, 2008; CH2MHILL, 2008). The septic system discharges into a shallow aquifer, also with a well-defined plume. The purpose of investigating these settings was to expand the existing literature on the occurrence and transport of PhACs in groundwater.

1.3 Organization of Thesis

This thesis has been organized into three chapters. The first chapter provides a brief introduction to the presence of pharmaceuticals in the environment. An introduction to the

pharmaceuticals that were studied, their presence in the environment, and the sites that were investigated are also provided.

Chapter 2 presents the findings of the study conducted at the septic system site. In this chapter, pharmaceutical concentrations observed in groundwater downgradient of the septic system are described. Particular attention is given to quality assurance and quality control (QA/QC), and a detailed discussion of the factors affecting the fate and transport of pharmaceuticals in both the saturated and unsaturated zones is provided.

Finally, Chapter 3 introduces the findings, both geochemical and pharmaceutical, at the two municipal landfills studied. A discussion relating to the transport properties of the pharmaceuticals in relation to a landfill hydrogeological setting is provided, and QA/QC measures employed are emphasized.

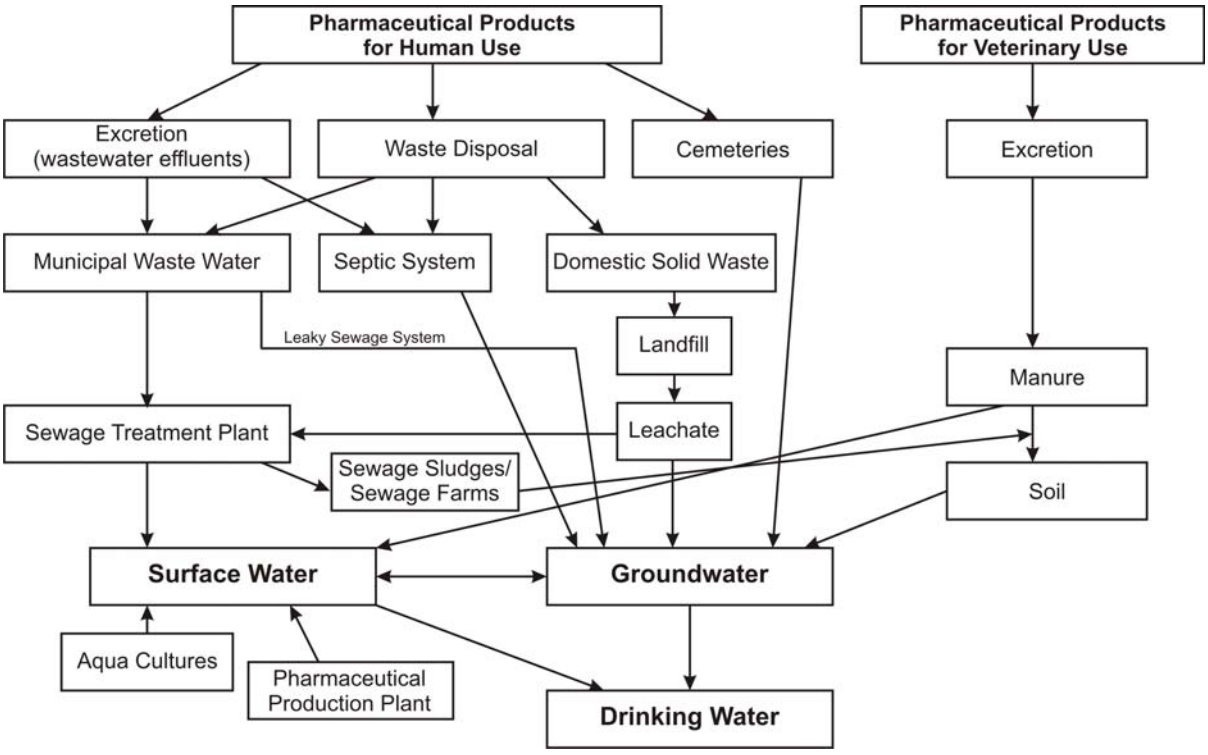


Figure 1.1 – Potential sources and transport pathways for pharmaceuticals in the environment. Adapted from a figure originally developed by Heberer (2002).

2.0 Presence of Pharmaceuticals in a Septic System Groundwater Plume

2.1 Introduction

Septic systems are a common method for treating and releasing wastewater, particularly in rural settings in North America. They are designed to treat the main contaminants of concern associated with septic beds: pathogens, organic carbon and ammonia (see Appendix A for details on septic system functioning). Until recently, little emphasis was placed on other contaminants of concern, including pharmaceutically active compounds (PhACs) (Godfrey et al., 2007; Carrara et al., 2008). Because many of these compounds are designed to have metabolic stability to function in the body, pharmaceuticals are often resistant to biodegradation and can therefore persist in the environment (Suntisukaseam et al., 2007). In addition, because of the large volumes used, they have been classified as environmentally relevant compounds (Scheytt et al., 2006).

The study of pharmaceuticals in groundwater has generally received less attention than pharmaceuticals in surface water, however, the number of studies focused on pharmaceuticals in groundwater has been increasing steadily. Some of the identified sources to groundwater include bank infiltration (Massmann et al., 2008), artificial groundwater recharge (Drewes et al., 2002), agricultural infiltration (Heberer et al., 1998; Scheytt et al., 2007; Siemens et al., 2008), landfills (Eckel et al., 1993; Schwarzbauer et al., 2002; Holm et al., 1995), and septic systems (Conn et al., 2006; Swartz et al., 2006; Godfrey et al., 2007; Carrara et al., 2008) (Figure 1.1).

2.1.2 Pharmaceuticals in Septic Systems

Recently, septic system plumes containing PhACs have been investigated. Swartz et al. (2006) studied the release of PhACs into a sand aquifer from a multi-resident property in the United States. Concentrations within the tank were as high as 23,000 ng L^{-1} for caffeine, and 65,000 ng L^{-1} for paraxanthine. These compounds were also detected several meters downgradient from the source, with a maximum groundwater concentration observed for caffeine of 1,710 ng L^{-1}. Conn et al. (2006) collected samples from 30 onsite treatment systems, 22 of which were septic tank-based. Analysis of tank samples indicated several pharmaceuticals in the 10's of μg L^{-1} range. A study conducted by Godfrey et al. (2007) found the presence of pharmaceuticals including carbamazepine and sulfamethoxazole at concentrations up to 450 ng L^{-1} in a shallow aquifer below a high school septic bed in Montana, USA. The same study also detected pharmaceuticals in groundwater below an urban area containing multiple residential tile beds at concentrations less than 25 ng L^{-1}, with the exception of caffeine that had a maximum concentration of 206 ng L^{-1}. More recently, Carrara et al. (2008) observed groundwater with elevated concentrations of several PhACs at two of three tile bed sites in Ontario, Canada. An evaluation of groundwater downgradient of a tile bed in Long Point, Ontario detected the presence of nine pharmaceutical compounds having maximum concentrations in the range of 20 to 12,000 ng L^{-1}. Five pharmaceutical compounds were detected in a plume downgradient of a tile bed at Lake Joseph, whereas at the third site, Point Pelee, Ontario, only two pharmaceutical compounds were observed at one shallow sampling point in the plume. While the number of studies is limited, it is apparent that septic systems are a source of pharmaceutical compounds to groundwater, and therefore potentially surface water and drinking water. The mechanisms controlling the

release and transport of pharmaceuticals in groundwater, however, are unclear and require further attention.

2.1.3 Pharmaceutical Disposal Patterns

There are a variety of methods in which pharmaceuticals are introduced to septic effluent, including direct disposal of unused or expired medications with the household's grey or black water. Multiple surveys conducted in the U.K. determined that approximately 10% of households surveyed had disposed of their PhACs in this manner (Bound et al., 2006; Slack et al., 2007). More importantly, however, pharmaceuticals may enter septic bed systems by excretion into wastewater either as a parent compound or as a metabolite (Ternes, 1998). The mass of excreted parent compound varies, depending on the structure of the drug, the mechanisms of the drug, the dosage or quantity, and the physiology of the individual (Bound and Voulvoulis, 2005). Typically only a small percent of the ingested drug is excreted in the unchanged form (Khetan and Collins, 2007; Siemens et al., 2008). The metabolized forms of the drugs which are excreted from the human body are often more reactive, more water soluble, and sometimes more toxic than the parent drug (Halling-Sørensen et al., 1998; Scheytt et al., 2007). Once in the environment, these metabolites may be modified further, or may revert to the original parent compound (Bendz et al., 2005). Predictions on the fate of PhACs in the environment require knowledge of usage rates, quantities excreted and/or disposed, transformation rates, and transport processes controlling both the parent compound and reaction products.

2.1.4 Purpose of Study

Pharmaceuticals and their metabolites may be introduced into a septic system through a variety of mechanisms. A number of studies have already identified that they can persist and enter into groundwater below and downgradient of tile beds (Conn et al., 2006; Swartz et al., 2006; Godfrey et al., 2007; Carrara et al., 2008). Because it is not uncommon for septic system plumes to eventually discharge to surface water bodies or near to drinking water supplies, it is important to understand where and how tile beds act as sources of PhACs as a way to ultimately understand the impact of such contaminants to groundwater, and consequently to human and aquatic health. In addition, because PhACs are able to be detected at such trace levels, the potential exists for their application as highly sensitive tracers of wastewater contamination.

2.2 Methods

The septic system at Long Point Provincial Park in Ontario, Canada has been extensively studied over the past 16 years (Robertson, 2008). The geology and chemistry of the site has been described previously (Aravena and Robertson, 1998; Robertson et al., 2000; Robertson, 2008; Carrara et al., 2008). The septic system at the site services a campground with approximately 200 overnight campsites, as well as patrons with day passes to the park. The park operates seasonally from May to November, and therefore for part of the year there is no loading to the tile beds. The single comfort station at the site is serviced by two tile beds, each approximately 290 m^2. The tile bed evaluated in this study has been used exclusively since 1990, with the exception of a two year period from 1995 - 1996 when the other tile bed was used. The tile bed drains into an aquifer that is 5 - 6 m thick, silt free with fine to coarse

primarily calcareous sand, overlaying a clayey silt aquitard. It has a hydraulic conductivity of 2 x 10^{-4} m s^{-1}, fraction of organic carbon (f_{oc}) of 0.15% wt., and a groundwater velocity in the area influenced by the septic effluent during loading of approximately 40 m yr^{-1} (Robertson, 2008). The septic plume extends southward into the moderately homogeneous sand aquifer with a low dispersivity, therefore the plume retains a large core zone that is relatively unaffected by dilution (Robertson, 2008). The plume eventually discharges into Lake Erie (Robertson, 2008).

2.2.1 Field Methods

Groundwater samples were collected on September 19, 2007 using a peristaltic pump connected to 0.64 cm (¼") diameter dedicated polyethylene tubing. The tubing sections were briefly purged, from 30 s to 1 minute, prior to collecting groundwater samples. The groundwater samples were filtered using 0.45 μm in-line Thermopor Membrane filters. Samples were collected for analysis of pharmaceuticals, anions, phosphate and ammonia. The pharmaceutical samples were collected in glass amber bottles in duplicate and acidified to a pH < 2 using 16N H_2SO_4. One sample was maintained at 4°C and the other frozen until analysis. Samples for PO_4 and NH_3/NH_4-N analysis were collected in high density polyethylene (HDPE) bottles and acidified using 16N H_2SO_4. Samples for anion analysis were also collected in HDPE bottles. Two sets of field blanks were collected. Blind duplicates were collected at four locations, or approximately one duplicate per 10 wells sampled.

2.2.2 Reagents

Drug standards for carbamazepine, gemfibrozil, naproxen, sulfamethoxazole, ibuprofen and caffeine were obtained from Sigma Aldrich Canada. For each analyte, a unique isotope-labelled internal standard was used. Table 2.1 outlines the unique internal standards used for each analyte, together with the properties of each analyte and internal standard. All internal standards were obtained from CDN Isotopes (Quebec, Canada) with the exception of sulfamethoxazole d_4 (Toronto Research Chemicals, Toronto, ON, Canada).

Nanopure water (Milli-Q water) was provided through the use of a 0.45 μm Millipore Q-Gard1 unit. High performance liquid chromatography (HPLC) grade methanol (MeOH) (99.9%), ammonium acetate, formic acid, acetic acid and acetonitrile were obtained from Caledon Laboratories Ltd. (Georgetown, ON, Canada).

All pharmaceutical stock solutions were prepared by measuring 10 mg of either an analyte or an internal standard and dissolving in MeOH/Milli-Q water (50:50 v/v), with the exception of gemfibrozil and its internal standard (gemfibrozil d_6), which were dissolved in 10% 0.03M NaOH in MeOH/nanopure water (50:50 v/v), and internal standards for ibuprofen and naproxen, which were dissolved in pure MeOH. The solvent selected was based on the solubility of each compound.

2.2.3 Sample Preparation

Samples stored at 4°C were allowed to reach room temperature. Frozen samples were allowed to thaw to room temperature, and were vacuum filtered using 0.45 μm nylon filters to prevent clogging of the solid phase extraction (SPE) cartridges by a gel residue that

formed as a result of freezing. A sorption study was conducted that evaluated the loss of the analytes onto the nylon filters. The results indicated that there was minimal to no sorption of all pharmaceuticals to the nylon filters (Hebig, 2008) and therefore it is not expected that this step will have affected the aqueous concentrations of the PhACs of interest. A laboratory blank was also prepared for each set of samples analysed.

One hundred mL of each sample was spiked prior to SPE with a mixture containing all six internal standards to achieve a concentration of 1 μg L^{-1} of each internal standard after the SPE step. Unique internal standards were utilized for each analyte to assess analyte losses during the SPE step and matrix suppression during analysis. Utilizing a unique internal standard for each pharmaceutical provides the most accurate representation of the unknown analyte to correct for losses during SPE, instrument suppression and other errors during analysis (Gros et al., 2007).

Solid phase extraction was performed using Oasis HLB 5 mL glass cartridges under approximately 13 cm (5 in.) Hg of vacuum. These cartridges have been used previously for PhAC analysis in environmental applications (Hao et al., 2006; Vanderford and Snyder, 2006; Feitosa-Felizzola et al., 2007; Gros et al., 2007; Díaz-Cruz et al., 2008). Cartridges were conditioned with 3 mL of HPLC grade MeOH and equilibrated with 3 mL Milli-Q water. The cartridges were loaded with the samples and washed using 3 mL of 5% MeOH (v/v). Finally, the cartridges were eluted with three repeats of 2 mL of MeOH. The eluate was collected in a glass amber bottle and stored at 4°C until time of analysis. Use of SPE cartridges serves two purposes, 1) impurities are removed from the samples, minimizing

instrument contamination and interferences during analysis, and; 2) the samples are concentrated, which improves detection limits. In this study, 100 mL of sample was concentrated to 6 mL, yielding a concentration factor of approximately 17. A set of blind spiked laboratory samples were prepared with analyte concentrations of 0.1 μg L^{-1}, 0.5 μg L^{-1}, and 1.0 μg L^{-1}. The purpose of these spiked samples was two-fold; 1) to evaluate the analysis and calibration of the MS/MS method, and 2) to evaluate the recovery of analytes and internal standards passing through the SPE cartridges.

Samples that were frozen were prepared within 3 months, and all samples extracted in MeOH were analyzed within 6 months. A cursory investigation of the impact of freezing samples and storing MeOH extracts on carbamazepine concentrations, presented in Appendix B, indicates that these processes did not affect the visual interpretation of carbamazepine plumes.

2.2.4 Pharmaceutical Analytical Methods

Analysis for pharmaceutical compounds was performed using HPLC electrospray tandem mass spectrometry (HPLC-ESI-MS/MS). The HPLC was an Agilent 1100 series operated using an eluant gradient. The mass spectrometer was an Applied Biosystems MDS SCIEX 4000QTrap. The nebulizer gas at the ionization source and the collision gas used to fragment the parent ion was N_2. A multiple reaction monitoring scan (MRM) was utilized for quantification, which occurred through a signal ratio between the analyte peak to that of the corresponding internal standard.

The analytical procedures utilized were modified from procedures described by Vanderford et al. (2003) and Stafiej et al. (2007). Analyses of caffeine, carbamazepine and sulfamethoxazole were conducted in positive ESI mode. A Symmetry RP18 column (Waters Corporation, Mississauga, ON, Canada) was used with a length of 50 mm, an internal diameter of 4.6 mm, and a particle size of 3 μm. The flow through the column was 1.25 mL min^{-1}, with an injection volume of 15 μL. Mobile phase A consisted of 5 mM ammonium acetate and 0.1 % formic acid in nanopure water. Mobile phase B was 100 % MeOH with 0.1 % formic acid. The gradient started at 15 % for mobile phase B, after 0.76 min increased to 100 %, then at 2.5 min decreased back to 15 % until 4 min was reached.

Naproxen, gemfibrozil, and ibuprofen were analysed in negative ESI mode. An XDB-C18 column (Agilent Technologies, Mississauga, ON, Canada) with a length of 150 mm, an internal diameter of 4.6 mm and a particle size of 5 μm was used. The flow rate through the column was 1 mL min^{-1}, with a total injection volume of 10 μL. Mobile phase A, at pH 4, was 30 % acetonitrile diluted with nanopure water with 6.9 mM acetic acid. Mobile phase B was 100 % acetonitrile. The gradient started at 0 % of mobile phase B, at 18 min increased to 3 %, at 22 min to 12 %, 40 min to 40 %, and ended at 45 min at 0 %.

2.2.5 Calibration

Instrument calibration was performed using an 8-point linear regression and a weighting factor of $1/x^2$, with a linear correlation coefficient of at least 0.999 (Table 2.2). The accuracies of most calibration standards used were 100 +/- 5% (Table 2.2). Accuracy is a measure of how close the calculated (measured) value was for each calibration standard, to

the expected concentration. The method detection limit (MDL) and limit of quantification (LOQ) were determined using a signal-to-noise ratio with a standard deviation of 3, where a signal to noise ratio of 3 was used to calculate the MDL and 10 was used to calculate the LOQ. Instrument detection limits are provided in Table 2.2, together with method detection limits that are corrected for the SPE concentration factor. The concentrations were determined using the external calibration curve by comparing the measured responses for the internal standards added to each sample to that of each analyte.

2.2.6 Geochemical Analytical Methods

Determinations of ammonia concentrations were made using automated colorimetric procedures at an external laboratory. Phosphate determinations were made spectrophotometrically with a HACH DR/2010 at 880 nm using the HACH ascorbic acid - molybdenum blue method. Anion concentrations were performed using ion chromatography.

2.3 Results and Discussion

2.3.1 Geochemical Analysis

Concentrations of major ions and nutrients were determined for all the piezometers sampled, and contour diagrams and depth profiles are presented in Figures 2.1 and 2.2, respectively. Tabulated results are provided in Appendix C. A total of five samples were analysed in duplicate for all geochemical parameters, for a total of 26 duplicate analyses. All duplicate analyses were similar to one another, with an average percent difference of 0.93% and a standard deviation of 1.1. Additional information on the geochemistry of the groundwater at the site is available in previous studies (Robertson and Harman, 1999; Robertson et al., 2000;

Robertson, 2008; Carrara et al., 2008). Concentrations of PO_4-P (up to 8.1 mg L^{-1}), NO_3-N (up to 98.25 mg L^{-1}) and Cl (up to 62.8 mg L^{-1}) were observed to be highest beneath and adjacent to the tile bed, decreasing further downgradient from the source. The Cl plume extends across the entire length (30 m) and depth (6 m below grade) of the cross section evaluated, maintaining a plume core across the distance of flow. Concentrations of Cl at the site decreased with distance from the source, however, the decrease in concentration of this conservative tracer was minimal, indicating that dispersive attenuation does not play a key role in this aquifer across the distance studied. This observation supports the findings of Robertson (2008), who observed a large core zone relatively unaffected by dilution, suggesting that the aquifer has a relatively low dispersivity.

Concentrations of NH_3/NH_4-N were below the detection limit (<0.01 mg L^{-1}) at the majority of piezometers sampled, particularly those that were deeper and/or further downgradient from the tile bed. These observations are similar to findings by Böhlke et al. (2006) who found that ammonium plumes tend to be small relative to those of other constituents, with highest concentrations observed closest to the source. The maximum NH_3/NH_4-N concentration detected was 11.6 mg L^{-1} in the piezometer nest at the edge of the tile bed. The concentrations of N species at Long Point are similar to those observed at another tile bed located in a similar geological setting (Ptacek, 1998). The behaviour of N species is closely related to the design of the septic bed (Appendix A). Ammonium is thermodynamically unstable in the oxidizing conditions present in the unsaturated zone. Therefore, within the unsaturated zone, NH_4 is oxidized to NO_3, which explains the presence of NO_3 in the plume, and the general absence of NH_3/NH_4-N. Ammonium also tends to exchange onto clay and

other mineral surfaces, leading to moderate attenuation relative to the average groundwater velocity (Böhlke et al., 2006; Repert et al., 2006), which could also contribute to the limited concentrations and travel distances relative to the conservative tracer Cl. A previous study conducted by Robertson (2008) identified that at the Long Point site, NH_4 was well oxidized and had limited presence in the piezometers closest to the tile bed, which our findings support. At depth and distance, NO_3 concentrations decline, likely as a result of removal through denitrification reactions, consistent with previous observations of denitrification in the Long Point aquifer (Aravena and Robertson, 1998).

Concentrations of SO_4 within the plume were variable. The highest concentrations were observed directly below the tile bed (84 mg L^{-1}), as well as at greater depths below the water table. Concentrations for Mn were fairly consistent throughout the entire plume, with highest concentrations observed closest to and directly below the tile bed. Elevated concentrations of Mn are attributed to release from mineral surfaces through reductive dissolution reactions as observed at other septic system sites (Ptacek, 1998).

The transport of PO_4 at the site has been well described by Robertson (2008). Elevated PO_4 concentrations were observed to be limited to shallow depths, with attenuation occurring away from the source zone (Figures 2.1, 2.2). Transport of PO_4 can be limited by adsorption/desorption and precipitation/dissolution reactions (Ptacek, 1998). Because PO_4 is negatively charged, positively charged mineral surfaces promote adsorption reactions. A sediment analysis by Robertson (2008) determined that the aquifer contains acid-extractable

Al, Fe, and Mn minerals, which could indicate that the presence of hydroxide minerals plays an important role in adsorption of PO_4.

2.3.2 Pharmaceutical Analysis

2.3.2.1 Quality Control and Quality Assurance

Pharmaceutical analyses were conducted along the cross section for caffeine, carbamazepine, sulfamethoxazole, gemfibrozil, naproxen and ibuprofen. Concentrations of all drugs analysed were consistently below detection in laboratory and field Milli-Q blanks prepared using the same SPE process employed for the unknown samples (Table 2.3), with the possible exception of caffeine at concentrations less than 1 ng L^{-1}, suggesting contamination within the instrument. However, because the background peak for caffeine was present in all samples, including the calibration standards, no correction beyond those obtained through the application of the calibration regression equation was required. Blank MeOH/Milli-Q samples spiked with internal standards for direct injection into the HPLC were below detection limits (Table 2.3) of all the target analytes, indicating there is no potential for contamination from the addition of the internal standards used.

Blind Milli-Q spiked samples prepared for quality control measures had high accuracies (91-110 %) for all drugs across a range of concentrations (100 to 1000 ng L^{-1}) (Table 2.3), indicating the accuracy of the calibration and analysis methods. The accuracy is calculated by comparing the measured concentration in the quality control samples, to the expected concentration.

2.3.2.2 Absolute Method Recovery

The absolute method recovery of the internal standards was expressed by comparing the peak area (counts) of the internal standard in a control set of Milli-Q spiked samples (method standards) passed through the SPE cartridges (n = 4) to MeOH/Milli-Q calibration standards (calibration standards) prepared for direct injection into the HPLC (Equation 2.1).

$$\text{Absolute IS Method Recovery (\%)} = \frac{\text{IS Peak Area in Method Standards}}{\text{IS Peak Area in Calibration Standards}} \times 100 \qquad (2.1)$$

In all unknown samples as well as the method standards, the internal standards were added prior to SPE, therefore the absolute method recovery is representative of the recovery of the SPE process, as well as the instrument detection capabilities. The method standards were prepared to have final analyte concentrations of 0.2, 0.5, 1.0, and 5.0 μg L^{-1}. The effect of passing samples through a nylon filter is expected to be negligible for all of the drugs, based on a sorption study which indicated little to no loss of the PhACs from the aqueous phase when in continued contact with the nylon filters (Hebig, 2008).

In addition, the absolute analyte recovery was calculated (Equation 2.2) for the method standards using the same method of comparing peak area in the method standards to peak area in the calibration standards (Table 2.4, Figure 2.3).

$$\text{Absolute Analyte Method Recovery (\%)} = \frac{\text{Analyte Peak Area in Method Standards}}{\text{Analyte Peak Area in Calibration Standards}} \times 100 \qquad (2.2)$$

The relative recovery of the analyte to internal standard was also calculated through Equations 2.3 and 2.4 to indicate the relation between internal standard recovery and calculated analyte concentration. The relative recovery ratio (Equation 2.3) was calculated

for both the method standards and the calibration standards and then used to calculate the relative method recovery (Equation 2.4).

$$\text{Relative Recovery Ratio} = \frac{\text{Analyte Peak Area}}{\text{IS Peak Area}} \times 100 \tag{2.3}$$

$$\text{Relative Method Recovery (\%)} = \frac{\text{Relative Recovery Ratio in Method Standards}}{\text{Relative Recovery Ratio in Calibration Standards}} \times 100 \tag{2.4}$$

The relative recovery is more reflective of the accuracy of the calibration and method, as it considers not only the internal standard recovery, but also the analyte recovery and therefore accounts for the internal standards that were used to calculate the final concentration of analytes in all samples.

Table 2.4 and Figure 2.3 illustrate the three parameters calculated for the absolute method recovery of the method standards. It is noted that ibuprofen (99 %), naproxen (86 %) and carbamazepine (86 %) had the best absolute recoveries of internal standards, however, the precision for all drugs ranged between 6 and 16 %. The internal standard absolute recovery for sulfamethoxazole was very high (140 %), however, the absolute recovery of the sulfamethoxazole analyte was also high (151 %), which resulted in a satisfactory overall relative recovery of 107 % (Table 2.4, Figure 2.3), illustrating the importance of utilizing an appropriate internal standard for each analyte.

For most of the pharmaceuticals studied, the absolute recovery of the internal standard in the method standards was similar to the absolute recovery of the corresponding analyte, which resulted in an acceptable relative recovery. Carbamazepine, sulfamethoxazole, caffeine, and ibuprofen all had relative recoveries in the range of 99 to 107 %. Naproxen and gemfibrozil

had higher relative recoveries (119 % and 122 % respectively), which indicates that measured values for these drugs could be elevated by approximately 20 % (Figure 2.3).

2.3.2.3 Internal Standard Recovery

Another recovery evaluation calculated considered the matrix effects of each individual sample, combined with the absolute method recovery. In this recovery, the peak area of the internal standard in all unknown samples was compared to the peak area of the internal standard in the calibration standards that were analysed together within a single group of samples (Equation 2.5).

$$\text{IS Recovery (\%)} = \frac{\text{IS Peak Area in Unknown Samples}}{\text{IS Peak Area in Calibration Standards}} \times 100 \qquad (2.5)$$

For drugs analysed in positive mode, carbamazepine had the lowest average recovery (69 %), with a relative standard deviation (%RSD), or precision, of 13 %, and sulfamethoxazole had the highest recovery (96 %) and also the highest %RSD (20 %) (Table 2.5). For the drugs analyzed in negative mode, average sample recoveries were between 84 and 97 %, but %RSDs were lower for all drugs (7-11%) (Table 2.5).

It is not unusual for environmental samples to have a high standard deviation in the recovery, because each sample has a unique matrix that will affect the recovery of the analytes on the SPE adsorbant, as well as the electrospray efficiency. Other studies investigating recoveries of drugs in environmental samples observed poor recoveries and high standard deviations for drugs (Hao et al., 2006; Pedrouzo et al., 2007). For blind spiked Milli-Q samples, recovery of internal standards for positive drugs were <80 %, however, high relative recoveries (97 – 107 %) indicate that the low internal standard recovery was compensated for in the final

calculation of the analyte concentration due to the addition of unique internal standards for each analyte. The relatively low or inconsistent recoveries of the internal standards in the samples (both environmental and blind spiked Milli-Q) could also be the result of peak distortion that typically occurs when the eluate that is injected into the HPLC is a stronger solvent than the mobile phase, or simply the result of variations in the operation of the instrument.

The relative recoveries of the blind Milli-Q spiked samples (99 - 109 %) (Table 2.5) indicate that the low recoveries of the internal standards were corrected through the use of isotope dilution techniques, given that the internal standard recoveries were similar to the unknown sample internal standard recoveries. Using a unique internal standard for each PhAC with similar recovery behaviour helps to correct for different recovery of each compound.

2.3.2.4 Pharmaceutical Findings

All six drugs analysed in this study were detected within the groundwater plume. The plume and depth profiles for each drug are presented in Figures 2.4 and 2.5, respectively. Plume and septic tank concentration are presented in Table 2.6. Carbamazepine and ibuprofen exhibited the overall highest concentrations and the furthest extent vertically and horizontally. Sulfamethoxazole and naproxen both had similar trends in that their highest concentrations occurred in the sampling points below the tile bed, and then decreased fairly abruptly downgradient. Concentrations of gemfibrozil were very low throughout the entire plume (10 ng L^{-1} to below detection limit (<1 ng L^{-1})). The highest concentrations measured in groundwater were carbamazepine (2,050 ng L^{-1}), sulfamethoxazole (1,990 ng L^{-1}) and

ibuprofen (1,790 ng L^{-1}). In the septic tank, the highest concentrations were observed for ibuprofen (29,350 ng L^{-1}) and caffeine (7,530 ng L^{-1}). The sample collected from the tank was not filtered in the field, and was only filtered during sample preparation, after being frozen. This method could account for the lower carbamazepine concentration of 77 ng L^{-1} in the tank relative to those observed within the groundwater plume (up to 2,050 ng L^{-1}). Alternatively, the plume may reflect previous conditions when tank concentrations of carbamazepine were higher, as the tank input is not considered constant at this site due to its seasonal operation and the varying population that it serves.

2.3.2.5 Partitioning, Sorption and Retardation Theory

The pharmaceutical compounds studied range from neutral compounds, to those that completely dissociate, and to those that are partially dissociated over the pH range of the field site (6.7 to 7.2 (Carrara et al., 2008)). The degree of compound dissociation is important when investigating the fate and transport of organic compounds, particularly when considering the degree of partitioning between solid and aqueous phases by sorption. The degree of sorption is affected by the pH of the system and the acid-base dissociation constant (pK_a) of each PhAC, and can be explained through parameters such as the octanol-water partitioning coefficient (K_{ow}), which is often used to estimate partitioning coefficients (K_d). When $pH > pK_a$, the PhACs in this study are dissociated into their anionic forms (Figure 2.6). This dissociation will influence the extent of sorption, as negatively charged compounds do not sorb as readily to soil particles and organic carbon (Haderlein and Schwarzenbach, 1993; Broholm et al., 2001). This relationship does not hold true for sorption to minerals, such as iron oxides, that are neutral or weakly positive at typical groundwater pH and therefore can

more readily sorb anionic organic compounds (Appelo and Postma, 2006). The influence of pH on K_d has been evaluated previously and it has been determined that for nonpolar compounds that are ionizable, pH influences the measured distribution of the compound between sorbed and aqueous phases (Haderlein and Schwarzenbach, 1993).

Knowledge of the aquifer properties at the field site is important in understanding the degree of electrostatic attraction that may exist between the neutral or dissociated PhACs, and the soil particles. Robertson (2008) performed sediment core analysis of the Long Point aquifer and determined that the aquifer sands are primarily calcareous, but also contain substantial amounts of acid-extractable Al, Fe, and Mn, which could indicate the presence of hydroxide minerals that may play an important role is sorption of negatively charged species. In addition, the amount of organic carbon present is 0.15 wt % (Aravena and Robertson, 1998).

2.3.2.5.1 Log D_{ow}

To express the relationship among K_{ow}, pH and pK_a, the log D_{ow}, which is a pH dependent partitioning coefficient, was calculated from pH 0 to 14 using the following equation (Figure 2.7) (Stuer-Lauridsen et al., 2000):

$$D_{ow} = \frac{K_{ow}}{1+10^{pH-pK_a}} \tag{2.6}$$

The pH range of relevance is that which exists at the site. Because the temporal and spatical variation in pH at the site is not large, the range of pH values considered is 6.7 to 7.2, as determined by Carrara et al. (2008). For some pharmaceuticals, particularly the acidic drugs that are dissociated under the pH conditions at the site, the log D_{ow} varies substantially from

the log K_{ow}. This difference has important implications on the fate and transport of the pharmaceutical compounds.

2.3.2.5.2 Retardation

By employing knowledge of the pH dependant partitioning coefficient, along with the site-specific aquifer properties, the retardation coefficient (*R*) was calculated for each PhAC for the pH range 0-14, and for the pH range at the site as obtained from Carrara et al. (2008) (Figure 2.7) using the following equation:

$$R = 1 + \frac{\rho_b}{n} K_d \tag{2.7}$$

where ρ_b is the aquifer bulk density, *R* is the retardation coefficient, and *n* is the effective porosity. As in Robertson (2008) an assumed bulk density of 2.65 g cm^{-3} and an effective porosity of 0.35 were used. The partitioning coefficient (K_d) was estimated using the following series of equations:

$$\log K_{oc} = 0.679 \log K_{ow} + 0.663 \tag{2.8}$$

as developed by Gerstl (1990) and recently employed by Löffler et al. (2005) in a similar pharmaceutical application. K_{oc} is the octanol-carbon partitioning coefficient, and K_{ow} is the octanol-water partitioning coefficient. In place of log K_{ow}, the log D_{ow} is employed, allowing retardation to be calculated dependent on the pH of the system. Finally, K_d is estimated based on the generalized expression:

$$K_d = K_{oc}\ f_{oc} \tag{2.9}$$

where f_{oc} is the fraction of organic carbon in the aquifer (0.15%, Aravena and Robertson, 1998). Depending on the equation selected to calculate the log K_{oc}, the actual value determined for *R* for each pharmaceutical varied slightly, however, the relative trends

remained the same, and it is therefore useful for qualitative comparison of relative transport distances. An examination of Figure 2.7 illustrates that *R* for all pharmaceuticals ranged from 1 to 6 over the pH range at the site, where ibuprofen carbamazepine and gemfibrozil had higher retardation coefficients than caffeine, naproxen and sulfamethoxazole.

2.3.2.6 Saturated Zone Transport

The septic plume extends southward into a moderately homogeneous sand aquifer (Robertson, 2008). Based on the measured Cl concentrations, dispersive dilution is not considered a significant process and therefore Cl can be assumed to behave conservatively. The conservative nature of Cl is important in evaluating the transport of the pharmaceutical compounds and noting the decrease in concentrations relative to that of Cl. This comparison provides an indication of which PhACs are attenuated by dispersive dilution only, and those that are more greatly attenuated are likely being affected by other processes, such as sorption or biodegradation. The concentrations of PhACs in groundwater are a direct reflection of the concentrations in the septic tank. Given the seasonal operation of the tile beds, combined with the varying population that the tank services, it is not likely a constant source for all the PhACs in this study. Not having a constant source concentration makes interpreting all plume delineations challenging, as trends observed within each plume could be either the result of attenuation processes, or simply reflect temporal variations in input concentrations. For the purpose of this analysis, it will be assumed that the tank concentrations were relatively constant to aid in the interpretation of the attenuation of each PhAC.

A visual comparison of the ibuprofen and carbamazepine concentrations to Cl indicates that these two drugs behave relatively conservatively in the saturated zone, which is consistent with previous studies in which carbamazepine was persistent in groundwater settings (Hua et al., 2003; Kreuzinger et al., 2004), as well as ibuprofen (Scheytt et al., 2005; Carrara et al., 2008). Concentrations observed at the site for carbamazepine were substantially higher than observed in previous studies investigating septic effluent in groundwater, as well as surface water and sewage effluent concentrations (Lissemore et al., 2006; Yu et al., 2006; Benotti and Brownawell, 2007; Godfrey et al., 2007; Gros et al., 2007). In this study, maximum groundwater concentrations for carbamazepine were in the range of thousands of ng L^{-1}. In the previous studies, observed concentrations were up to 16.2 ng L^{-1} (Lissemore et al., 2006) and 98.9 ng L^{-1}(Yu et al., 2006) in surface waters receiving urban inputs, 65 ng L^{-1} in sewage effluent (Benotti and Brownawell, 2007), and between 60 – 210 ng L^{-1} in groundwater (Godfrey et al., 2007).

Carbamazepine is a basic compound, characterized by a high pK_a (Figure 2.6; Table 2.1), indicating that it is not dissociated over the pH range at the site. It is moderately hydrophobic (log K_{ow}=2.45). Hydrophobic sorption is therefore expected to be an important sorption mechanism for this compound (Scheytt et al., 2005). However, a previous laboratory study investigating sorption of carbamazepine onto Long Point sand found that given the nature of the sand (f_{oc} = 0.15%; Robertson, 2008), carbamazepine had a preference for the aqueous phase, and therefore sorption was minimal and the drug behaved nearly conservatively (Seibert, 2007).

Concentrations of ibuprofen in groundwater at the Long Point site (up to 1,790 ng L^{-1}) were at least one order of magnitude higher than reported previously in surface water (150 ng L^{-1}) (Gros et al., 2007), and were more similar to concentrations observed for sewage effluent (870 – 85,000 ng L^{-1}) (Heberer, 2002), possibly due to photolytic degradation in surface water environments. In contrast to carbamazepine, ibuprofen has a low pK_a (Figure 2.6) and is therefore present at the site in a predominantly dissociated form, which indicates that in addition to hydrophobic sorption, other processes may influence the transport of ibuprofen as a result of its anionic form. Based on its log K_{ow} partitioning coefficient (3.97) and the relatively high calculated retardation factor, one would expect that ibuprofen would undergo a moderate to high degree of sorption, and would be greatly attenuated, however, this is not what was observed. In a laboratory sand column study conducted by Scheytt et al. (2005), it also was determined that ibuprofen had a much higher mobility than would be expected based solely on the octanol-water partitioning coefficient. These findings may be explained by Siemens et al. (2008), who identified that for acidic pharmaceuticals dissociated into their anionic form, sorption to negatively charged particles, such as the organic fraction of sand, is impeded by repulsive electrostatic forces. This finding is supported by the log D_{ow} values calculated for ibuprofen of 2.17 to 1.68 across a pH range 6.7 to 7.2 (Figure 2.7), which are significantly lower than the log K_{ow} value of 3.97 for the pH range present at the field site, and therefore suggests a lower sorption potential. The slightly lower mobility of ibuprofen relative to that observed for carbamazepine in this field setting may be the result of sorption of the negatively charged drug to positively charged sediment surfaces. Alternatively, it could be the result of temporal changes in tank concentrations for these two PhACs.

Gemfibrozil was not observed at elevated concentrations at any location sampled (Figures 2.4, 2.5). The concentrations observed for gemfibrozil in groundwater in this study (1 – 10 ng L^{-1}) were generally lower than concentrations reported for treated sewage effluent (up to 2,500 ng L^{-1}) (Gros et al., 2007), surface waters (10-130 ng L^{-1}) (Yu et al., 2006; Gros et al., 2007), and groundwater (2 – 1960 ng L^{-1}) (Carrara et al., 2008). Like ibuprofen, gemfibrozil is an acidic compound with a moderate to high log K_{ow} (4.77) (Table 2.1), and therefore transport of gemfibrozil is expected to be similar to ibuprofen. Concentrations for gemfibrozil were low throughout the entire plume, and it did not appear to attenuate greatly along the distance investigated, assuming a relatively constant input concentration. Like ibuprofen, over the pH range for the site, gemfibrozil is present in its anionic form, suggesting a lower sorption potential than would be expected if only the log K_{ow} was considered. At some of the sampling locations downgradient of the tile bed, concentrations were higher than concentrations closer to the source, which are similar to findings of Siemens et al. (2008). Bendz et al. (2005) also observed a similar increase in concentrations of gemfibrozil along a river flow path, and attributed the increase to reversion of excreted metabolites back to the parent compound. In human urine, gemfibrozil is excreted as approximately 70% metabolites, and only 6% unchanged as the parent compound (Siemens et al., 2008). This study did not involve analysis of metabolites. Alternatively, the higher concentrations may reflect temporal variations in discharge rates or complex geochemical conditions.

Sulfamethoxazole concentrations in this study (average of 225 ng L^{-1}, up to 1,990 ng L^{-1}) were slightly higher than other groundwater findings for septic effluent plumes (10 – 450 ng

L^{-1}) (Godfrey et al., 2007), but were within the same order of magnitude as observed in a previous investigation of groundwater (Godfrey et al., 2007). An overview study indicated that sulfamethoxazole has been observed in a variety of groundwater settings in concentrations ranging from trace, up to 450 ng L^{-1} (Heberer, 2002), indicating that this drug is persistent in a variety of groundwater settings. Sulfamethoxazole is an acidic compound characterized by a low log K_{ow} (0.89), which results in a lower log D_{ow} (0.59 to -7.11 over the pH range of 6 to 14) (Figure 2.7). As a result, it would be expected that sulfamethoxazole would have a high mobility. The calculated retardation factor also indicates a high mobility. In this study, sulfamethoxazole concentrations were observed to decrease fairly abruptly downgradient from the source area. This observation is consistent with field and laboratory studies conducted previously, which determined that sulfonamides actually have a high degree of initial sorption (Stoob et al., 2007; Wehrhan et al., 2007). Sulfonamides have two ionizable functional groups that affect transport in the environment, however, only the neutral and anionic forms are significant in the pH range at the Long Point site (Tappe et al., 2008). It was found that uptake by cells for biodegradation is substantially higher for neutral species than charged (Tappe et al., 2008). Sulfamethoxazole is neutral in its undissociated form, but given the pK_a (Figure 2.6), very little of the drug would exist in the undissociated form, therefore it is unlikely that biodegradation plays a key role in the saturated zone for attenuation of sulfamethoxazole.

Naproxen and caffeine appear to be the most highly attenuated of the drugs analyzed, if constant tank concentrations are assumed. Concentrations of naproxen were substantially lower than observed in previous studies investigating septic effluent in groundwater, surface

water and sewage effluent (Lissemore et al., 2006; Yu et al., 2006; Benotti and Brownawell, 2007; Godfrey et al., 2007; Gros et al., 2007). In this study, maximum concentrations for naproxen were in the range of hundreds of ng L^{-1}. In previous studies, concentrations were in the range of 41.7 ng L^{-1} (Lissemore et al., 2006) in surface waters, and 380 ng L^{-1} in sewage effluent (Yu et al., 2006). Based on its pK_a (Table 2.1, Figure 2.6), naproxen is nearly completely dissociated into ionic components, resulting in a lower log D_{ow} across the pH range at the site (Figure 2.7). While the ionic form of naproxen would not be electrostatically attracted to the predominantly negatively charged soil and organic matter particles in the Long Point aquifer, there is potential for sorption onto iron oxides present in the aquifer material (Roberston, 2008). It is likely that other processes are responsible for the high degree of attenuation given that the calculated retardation coefficient (Figure 2.7) for this PhAC is so low. A possible explanation is that biodegradation may be playing a key role in the attenuation process of naproxen. Tappe et al. (2008) proposed that drugs that are not sorbed to soil particles and remain in the aqueous phase are generally more biologically available, and potentially more prone to degradation reactions.

Concentrations for caffeine were notably lower than previously reported concentrations for septic tank effluent, municipal sewage effluent, groundwater, and surface waters (Swartz et al., 2006; Conn et al., 2006; Benotti and Brownawell, 2007). Concentrations of caffeine observed in this study were also markedly lower than a previous groundwater study that observed caffeine in a shallow monitoring well below an urban subdivision contaminated with domestic waste water, with concentrations up to 230 ng L^{-1} (Seiler et al., 1999). This study by Seiler et al. (1999) determined that from a variety of wells sampled, the deeper

wells and wells further from the source did not have measurable concentrations of caffeine, even though some were contaminated by wastewater, as indicated by elevated NO_3 concentrations. The findings at Long Point also indicate that in groundwater, caffeine is more readily attenuated than some of the other pharmaceuticals evaluated, assuming a constant source concentration. The pK_a (10.4) and calculated R value (1) suggest that caffeine would not be dissociated in this environment, and hydrophobic sorption would be minimal. As a result, the observed losses may be due to biodegradation reactions. Bioavailability and uptake by cells is dependant on the ionic charge, where uptake by cells is much greater for neutral species than charged (Tappe et al., 2008), and therefore uptake of the neutral parent compound of caffeine may be a significant process in this system.

To summarize, in the saturated zone all drugs showed at least some degree of attenuation when comparing groundwater concentrations to Cl concentrations and using the assumption that tank concentrations for these PhACs are relatively constant. Dispersive dilution is a relatively insignificant process in the aquifer across the distance studied, and therefore, other processes such as hydrophobic or electrostatic sorption, and chemical degradation and biodegradation reactions would contribute to the attenuation of the non-conservative drugs. As attenuation was difficult to predict by examining properties such as the pK_a, log D_{ow} and *R*, other processes such as ion exchange, more complex adsorption reactions and degradation reactions may be important in determining fate and transport interpretation. In addition, variability in PhAC concentrations throughout each plume could be the result of temporal changes in input (septic tank) concentrations. Further studies such as column investigations

and additional sampling to obtain temporal tank concentrations would assist in delineating specific processes that affect transport of PhACs in this aquifer system.

2.3.2.7 Unsaturated Zone Transport

While the focus of this study was not on the unsaturated zone, the drugs leaching from the septic tank passed through the unsaturated zone prior to entering the groundwater system, which affected their fate and transport. Studies pertaining to unsaturated, aerobic conditions indicate that, in general, pharmaceuticals show higher elimination and lower mobility under unsaturated conditions than during saturated transport (Scheytt et al., 2006). The Long Point site is characterized by a shallow water table, which did not allow full removal prior to the wastewater recharging the water table, however, the decline in concentrations of the pharmaceuticals between the tank and the first sampling point (Table 2.6), clearly indicates that many drugs exhibit a much larger decrease in concentration across the unsaturated zone than the conservative tracer (Cl), indicating that degradation and/or sorption processes are playing a large role in the fate and transport of these PhACs in the unsaturated zone. This analysis is based on the assumption that the tank concentrations are constant. Based on the presence of NO_3 in the plume, it is apparent that the NH_4 in the septic tank is oxidized as it passes through the unsaturated zone, suggesting oxygen is present and therefore available for biodegradation and or oxidation reactions in the unsaturated zone.

Another important consideration in the attenuation of all pharmaceuticals passing through the unsaturated zone is the pH of the system. In many septic systems, including the tile bed at Long Point (Carrara et al., 2008), the pH is lowest in the groundwater closest to the tile beds

(Zanini et al., 1998). The low pH is the result of the nitrification reaction that occurs in the unsaturated zone, which yields two moles H^+ for every one mole of NH_4^+ oxidized into NO_3^-:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \quad (2.10)$$

It can be assumed that the pH in pore water in the unsaturated zone is even lower than in the groundwater zone, which may have implications on the transport of pharmaceuticals in the vadose zone, because as calculated previously (Figure 2.7), retardation is shown to increase with decreasing pH. Therefore, in addition to biodegradation in the aerobic unsaturated zone, processes controlled by the pH, including enhancement of hydrophobic sorption processes due to less extensive dissociation, and for those drugs that dissociate at low pH, electrostatic sorption of anionic pharmaceuticals onto cationic surfaces in the aquifer, may play a key role in their attenuation.

The tank sample was not filtered in the field, and therefore it is also possible that the concentrations obtained are not entirely indicative of the aqueous concentrations. For example, when the samples were acidified and the pH of the water was modified, this could have either increased sorption to colloidal matter, or caused desorption due to changes in partitioning preferences. For the purpose of this interpretation, it is assumed that the concentrations obtained are representative of actual, constant aqueous concentrations in the tank. It is, however, recognized that tank concentrations may not be constant as a result of a varying population which the septic system serves.

Under anaerobic conditions, such as those that would be present in the tank, the biological transformation of most PhACs is hindered (Siemens et al., 2008), which could explain why

for many drugs, the concentrations were higher in the tank than those measured in the aquifer. Ibuprofen, naproxen and caffeine were the PhACs that had the highest concentrations in the tank (Table 2.6). All were orders of magnitude higher than concentrations found in groundwater, indicating extensive removal of these PhACs within the unsaturated zone. Naproxen is excreted in urine as 10% of the parent compound (Siemens et al., 2008), which explains the high tank concentration. Of all the PhACs studied, caffeine had the highest solubility, and also the second highest concentration in the tank, which is not surprising given the high consumption of caffeine in beverages (Table 2.1).

Previous laboratory studies performed using unsaturated, aerobic sand columns determined that ibuprofen had a retardation factor of 3.0 (assuming linear sorption), and a high degree of attenuation during transport that could partly be attributed to biodegradation (Scheytt et al., 2006). Column studies conducted by Scheytt et al. (2007) indicated that ibuprofen is significantly retarded and transformed during passage through the unsaturated zone. In the field, the concentrations of ibuprofen decreased markedly between the tank and the shallow groundwater (Table 2.6), indicating a high degree of removal in the unsaturated zone, which is consistent with the laboratory studies by Scheytt et al. (2007).

Concentrations of sulfamethoxazole also decreased between the tank and the water table, however, the decrease was substantially less than that documented by Godfrey et al. (2007), who observed a decrease in concentrations of 15-1,200 times during passage through a 2 m thick, sandy unsaturated zone. This difference could be the result of the tank concentration for sulfamethoxazole not being entirely representative as a result of not being filtered prior to

sample preservation, or to less effective removal processes in the unsaturated zone. The difference could also indicate that tank concentrations for sulfamethoxazole are not constant.

The concentrations of carbamazepine in the tank are lower than in the groundwater, preventing an estimate of removal rates. The higher concentrations in groundwater may be indicative of variations in the tank concentrations. However, previous laboratory scale studies under unsaturated conditions in sand found that carbamazepine showed minimal degradation and sorption, and that the unsaturated zone shows less elimination than saturated transport (Scheytt et al., 2006). Riverbank filtration studies also showed that carbamazepine attenuation was minimal (Osenbruck et al., 2007). Drewes et al. (2002) found that antiepileptic drugs persist during groundwater recharge. The low pH in the unsaturated zone below the tile zones would not support sorption of this neutral compound. Therefore, it is likely that minimal attenuation would have occurred in the unsaturated zone in this aquifer, particularly given the limited thickness of the vadose zone.

2.3.2.8 Significance of Findings

Because it is not uncommon for plumes from septic systems to eventually discharge to surface water bodies or to be captured by nearby drinking water supplies, it is important to understand where and how tile beds act as sources of PhACs as a way to ultimately understand the impact of such contaminants on groundwater and drinking water supplies. In this study, several of the pharmaceuticals were detected in groundwater at distances as far as 30 m from the tile beds. These observations have implications for Ontario drinking water and well installation regulations. According to the Ontario Water Resources Act (R.R.O.

1990, Regulation 903), any new, undrilled well must be at least 30 m from a potential source of contamination, such as a tile bed. The findings in this study indicate the possibility that drugs, such as carbamazepine and ibuprofen, could be found in drinking water supplies for water wells located 30 m from septic system tile beds. The likelihood of drugs entering drinking water supplies would be further enhanced in settings where groundwater velocities would be increased due to high rates of groundwater withdrawal or high loading from tile beds. Concentrations for these PhACs were in the $\mu g\ L^{-1}$ range in groundwater, markedly lower than maximum daily adult dosages which range from1,200 to 3,200 mg for the PhACs in this study (RxList Inc., 2008). While the groundwater concentrations found in this study appear to pose little risk to adults when considering typical daily dosages, the same may not be true for fetuses or children who are more vulnerable to low PhAC exposure given the nature of their development and metabolic systems. Children have been found to have a greater risk of adverse effects resulting from exposure to PhACs, and also have the potential risk of being exposed to PhACs not designed for pediatric care (Collier, 2007). Additionally, unintentional exposure of PhACs in trace concentrations can be harmful to pregnant women and their developing fetus. Over the course of a pregnancy, women are inadvertently exposed to a number of drugs that are capable of causing birth defects, and it has been estimated that women can ingest close to thirteen percent of a single dose over a 36 week period (Collier, 2007). In addition, the ability for PhACs to have additive effects identifies the possibility for concentrations to be considered environmentally relevant to a variety of other organisms. Finally, this study suggests that PhACs may be used as highly sensitive tracers or indicators of urban pollution.

2.4 Conclusions & Recommendations

The septic system at the Long Point Provincial Park acts as a source of the pharmaceutical compounds carbamazepine, ibuprofen, naproxen, caffeine, sulfamethoxazole and gemfibrozil to groundwater. The drug that appeared to be the most persistent and recalcitrant in this environmental setting was carbamazepine, with detections as far as 30 m from the septic bed infiltration zone. However, in the saturated zone all drugs showed at least some degree of attenuation, with ibuprofen, naproxen, caffeine, gemfibrozil and sulfamethoxazole being more greatly retarded along the primary groundwater flow direction than carbamazepine. This assessment of attenuation assumes a constant source, and is affected by the varying detection limits of each PhAC. Maximum groundwater concentrations were 2,050 ng L^{-1} (carbamazepine), 1,990 ng L^{-1} (sulfamethoxazole), 160 ng L^{-1} (caffeine), 1,790 ng L^{-1} (ibuprofen), 625 ng L^{-1} (naproxen) and 10 ng L^{-1} (gemfibrozil). Dispersive dilution was found to be a relatively minor process in the aquifer across the distance studied, and therefore, other processes likely contribute to the attenuation of these non-conservative drugs. As attenuation was difficult to predict by examining properties such as the pK_a, log D_{ow} and *R*, other processes such as ion exchange or more complex adsorption reactions and the potential for degradation may be important in determining fate and transport interpretation. Consideration of the degree of dissociation of each pharmaceutical compound was also considered relevant in this investigation. Further studies such as column investigations would assist in delineating specific processes that affect transport of PhACs in this and other aquifer systems. Analysis of additional tank samples would provide an indication of the constancy in tank concentrations.

A brief investigation of transport across the unsaturated zone illustrated that most of the drugs exhibit a much larger decrease in concentration across the unsaturated zone than the conservative tracer (Cl). This interpretation assumes relatively constant concentrations for all PhACs within the septic tank. In particular, ibuprofen, caffeine and naproxen had the greatest difference in concentrations between the tank and the groundwater, suggesting a high level of removal in the unsaturated zone. Therefore, degradation, biodegradation and/or sorption processes play an important role in the fate and transport of these PhACs in the unsaturated zone. As a result, additional laboratory and field studies on this subject are recommended, as in most environmental settings, contaminants pass through the unsaturated zone prior to entering the groundwater systems.

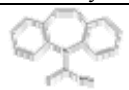
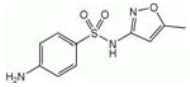
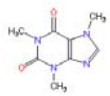
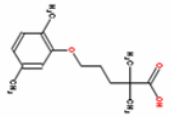
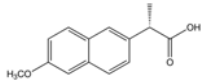
	Drug Class	CAS No.	Molecular Formula	Chemical Structure of Analyte	Molecular Weight g mol^{-1}	log K_{ow}	Solubility (mg L^{-1})	pK_a
Carbamazepine Carbamazepine d_{10}	Anticonvulsant, antidepressant	298-46-4 132183-78-9	$C_{15}H_{12}N_2O$ $C_{15}H_2N_2OD_{10}$		236.27 246.33	2.45	17.7	13.9
Sulfamethoxazole Sulfamethoxazole d_4	Antibiotic	723-46-6 n/a	$C_{10}H_{11}N_3O_3S$ $C_{10}H_7D_4N_3O_3S$		253.28 257.3	0.89	610	6
Caffeine Caffeine d_3	Stimulant	58-08-2 26351-03-1	$C_8H_{10}N_4O_2$ $C_8H_7N_4O_2D_3$		194.19 197.21	-0.07	21,600	10.4
Gemfibrozil Gemfibrozil d_6	Lipid regulator	25812-30-0 25812-30-0	$C_{15}H_{22}O_3$ $C_{15}H_{16}O_3D_6$		250.33 256.37	4.77	19	4.75
Naproxen Naproxen ^{13}C	Non-steroidal anti-inflammatory	22204-53-1	$CH_3OC_{10}H_6CH(CH_3)CO_2H$		230.26	3.18	15.9	4.15
Ibuprofen Ibuprofen d_3	Non-steroidal anti-inflammatory	15687-27-1 121662-14-4	$C_{13}H_{18}O_2$ $C_{13}H_{15}O_2D_3$		206.28 209.3	3.97	21	4.91

Table 2.1 – Pharmaceuticals of interest, along with their chemical properties (Trenholm et al., 2006) and structures. Also provided are the names, CAS number, molecular structure and molecular mass of the internal standards paired with each analyte.

	HPLC Mode of Analysis	Range of Calibration ($\mu g\ L^{-1}$)	Linear Correlation Coefficient (r^2)	Range of Accuracy of Calibration (%)	Instrument MDL/LOQ ($ng\ L^{-1}$)	Method MDL/LOQ (ng/L)
Carbamazepine	Positive	0.1 - 20	0.9996	96-104	3/37	0.2/2.2
Sulfamethoxazole	Positive	0.1 - 20	0.9995	95-105	23/78	1.4/4.6
Caffeine	Positive	0.1 - 20	0.9995	94-104	0/20	0/1.2
Gemfibrozil	Negative	0.1 - 20	0.9995	95-107	15/65	0.9/4
Naproxen	Negative	0.1 - 20	0.9994	95-105	139/763	8/45
Ibuprofen	Negative	0.1 - 60	0.9994	92-109	189/648	11/38

Table 2.2 – Method Calibration. For all the drugs analysed in negative ESI mode, selected samples were analyzed using three separate calibrations. The information provided is representative of all three analysis runs. All calibrations were performed using a linear regression with at least 8 calibration points, and a weighting factor of $1/x^2$. The accuracy of the calibrations illustrates how close the measured concentration of each standard was to the expected concentration. The instrument method detection limit (MDL) and limit of quantification (LOQ) indicate the sensitivity of the analytical method. The Method MDL and LOQ have been corrected for the concentration factor that resulted during the solid phase extraction process.

	Accuracy of Blind Spikes (%) and %RSD	Blanks (Lab and Field, and blanks spiked with Internal standards)	Per cent Difference of Duplicates
Carbamazepine	100 +/- 3	$< 0.2\ ng\ L^{-1}$	0.4 +/- 0.4
Sulfamethoxazole	101 +/- 2	$< 1.4\ ng\ L^{-1}$	4.3 +/- 5.1
Caffeine	101 +/- 3	trace peak	3 +/- 4.3
Gemfibrozil	117 +/- 10	$< 0.9\ ng\ L^{-1}$	8.2 +/- 5.9
Naproxen	103 +/- 10	$< 8\ ng\ L^{-1}$	4.8 +/- 4.2
Ibuprofen	102 +/- 7	$< 11\ ng\ L^{-1}$	2.8 +/- 3.2
	n = 3		n = 3

Table 2.3 – Quality Assurance and Quality Control. The accuracy of the blind spiked samples were measured by comparing the measured concentration to the expected concentration. Blank samples were analysed throughout each analytical run. The average percent difference between duplicates samples was calculated, and the standard deviation is provided. Sample sizes (n) are noted.

	Recovery of IS in Method Standards (%)	% RSD	Recovery of Analyte in Method Standards (%)	% RSD	Relative Recovery in Method Standards (%)	% RSD
Carbamazepine	86	8	86	9	99	7
Sulfamethoxazole	140	9	151	17	107	7
Caffeine	116	6	126	6	107	2
Gemfibrozil	82	16	101	21	122	9
Naproxen	86	16	103	26	119	20
Ibuprofen	99	13	102	16	102	7
	n = 4		n = 4		n = 4	

Table 2.4 – The absolute recovery of each internal standard (IS), analyte and relative recovery, and the per cent relative standard deviation (%RSD) is noted for method standards. Method standards were prepared at four analyte concentrations (0.2, 0.5, 1.0, 5.0 μg L^{-1}) and consisted of Milli-Q samples spiked prior to SPE with analytes and internal standards. Absolute IS recoveries was determined by comparing the peak area of the internal standard in the method standards, to the peak area of the internal standard in the calibration standards. For recovery of the analyte, the same practice was employed by comparing analyte peaks rather than internal standard peaks. In addition, the relative recovery, which considers the ratio of the analyte to that of the internal standard is provided for the method standards, which is representative of the final accuracy in the calculation of analyte concentrations. Sample sizes (n) are noted.

	Sample Recovery of IS (%)	%RSD	Relative Recovery of Blind Spikes (%)	%RSD
Carbamazepine	69	13	100	4
Sulfamethoxazole	96	20	100	2
Caffeine	89	16	102	2
Gemfibrozil	97	7	109	2
Naproxen	84	7	99	11
Ibuprofen	90	11	99	12
	n = 41		n = 3	

Table 2.5 – Sample recovery data. The recovery of each internal standard (IS), and the percent relative standard deviation (%RSD) is noted for all unknown samples. Recovery was determined by comparing the peak area of the internal standard in unknown samples, to the peak area of the internal standard in the calibration standards. In addition, the relative recovery, which considers the ratio of the analyte to that of the internal standard is provided for the blind spiked samples, which were a set of quality control standards spiked to known analyte concentrations, and then processed through solid phase extraction (SPE) and HPLC-MS/MS analysis. Samples sizes (n) are noted.

Sample Location	Sample Depth (m bgs)	CBZ ng L^{-1}	SMX ng L^{-1}	CAF ng L^{-1}	IBU ng L^{-1}	NAP ng L^{-1}	GEM ng L^{-1}
Tank		77	635	7530	29350	1235	< 1
LP-120	2.8	19	11	20	336	< 8	8
	2.8	19	11	-	337	< 8	8
	3.4	460	316	11	231	12	9
	3.9	1070	207	47	618	121	1
	4.6	747	196	19	265	40	<1
	5.3	476	< 1.4	< 1	12	< 8	<1
LP-121	2.6	291	22	9	19	< 8	< 1
	3.2	771	455	< 1	116	31	2
	3.8	1280	600	48	18	43	5
	4.4	829	706	54	1210	151	1
	5	835	4	46	233	7	1
LP 122	2.8	460	478	66	3	< 8	< 1
	3.4	929	92	14	14	19	1
	4.6	959	323	106	33	39	1
	5.2	-	-	-	-	-	-
LP-123	2.6	435	255	19	7	< 8	< 1
	3.2	824	86	2	107	52	2
	3.8	1510	560	77	1790	309	9
	4.5	16	7	9	117	88	3
LP-138	1.9	788	26	13	3	< 8	< 1
	2.3	2050	1990	159	870	624	5
	2.7	408	6	6	759	23	6
	3.1	564	9	7	624	88	10
LP-136	1.9	40	14	11	< 11	< 8	< 1
	2.3	431	46	32	8	15	1
	2.7	465	58	20	12	32	1
	3.1	-	-	-	-	-	-
LP-124	1.6	22	9	< 1	5	< 8	< 1
	2.1	173	33	2	4	< 8	< 1
	2.6	134	< 1.4	9	19	< 8	< 1
	3.1	103	3	2	4	< 8	< 1
	3.6	155	< 1.4	48	21	< 8	< 1

Table 2.6 – Concentrations of the pharmaceuticals carbamazepine (CBZ), sulfamethoxazole (SMX), caffeine (CAF), ibuprofen (IBU), naproxen (NAP) and gemfibrozil (GEM) in groundwater and the septic tank at the Long Point septic system plume. If not detected, concentration is listed to be below the method detection limit (MDL). If sample was not processed, a '-' is denoted. Peizometer nests are arranged based on proximity to the tile bed.

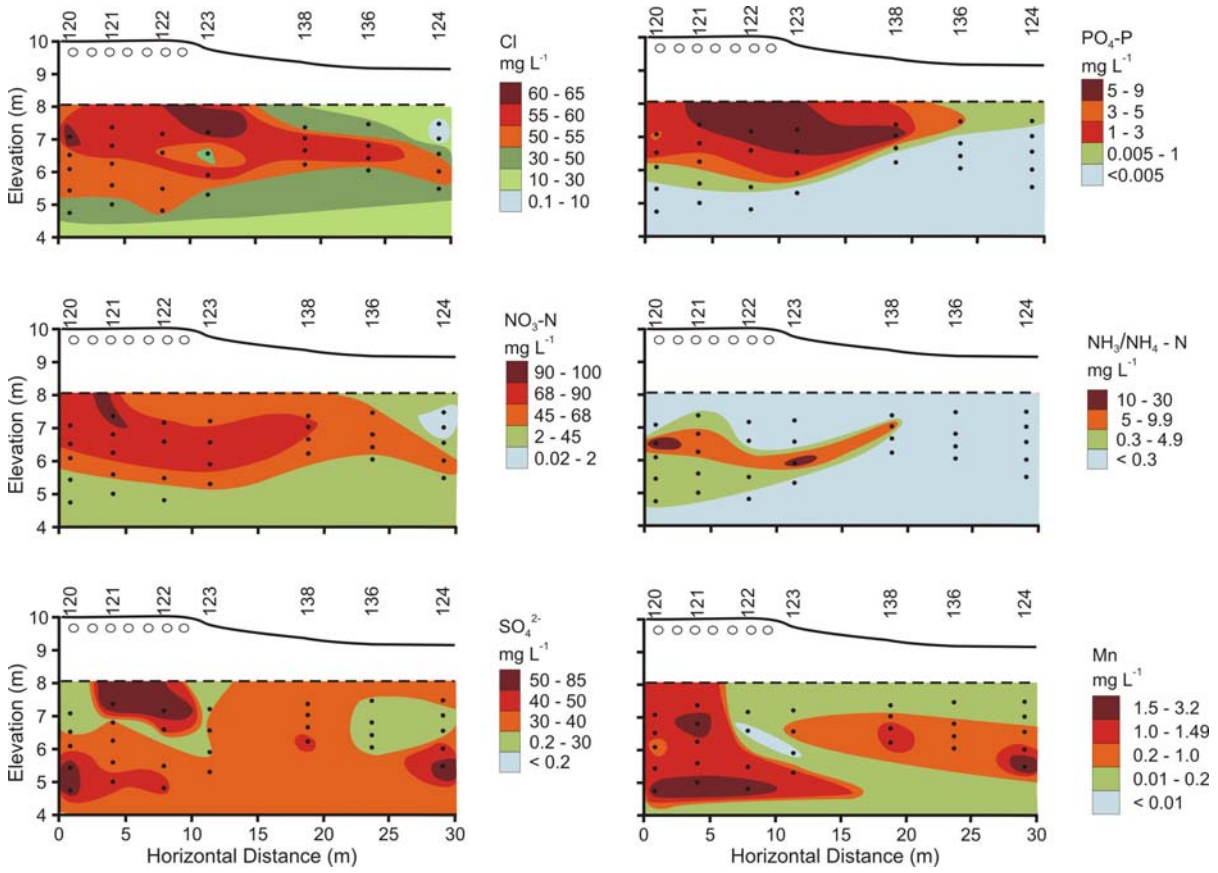


Figure 2.1 – Geochemical parameters in the groundwater downgradient of the Long Point septic tile bed. Concentrations are in mg L^{-1}.

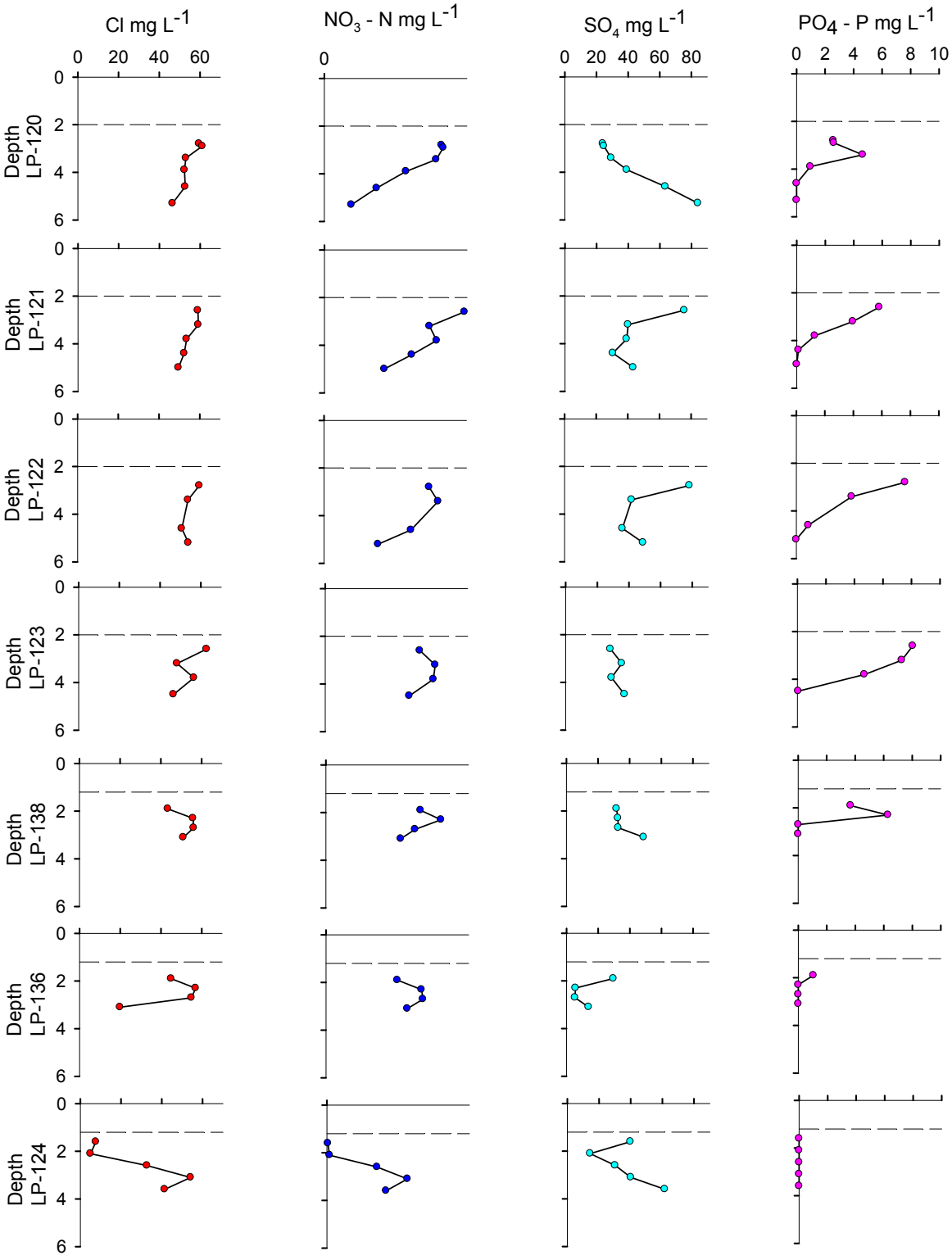


Figure 2.2 – Depth (m) profiles for geochemical parameters at sampling points downgradient of the Long Point septic bed.

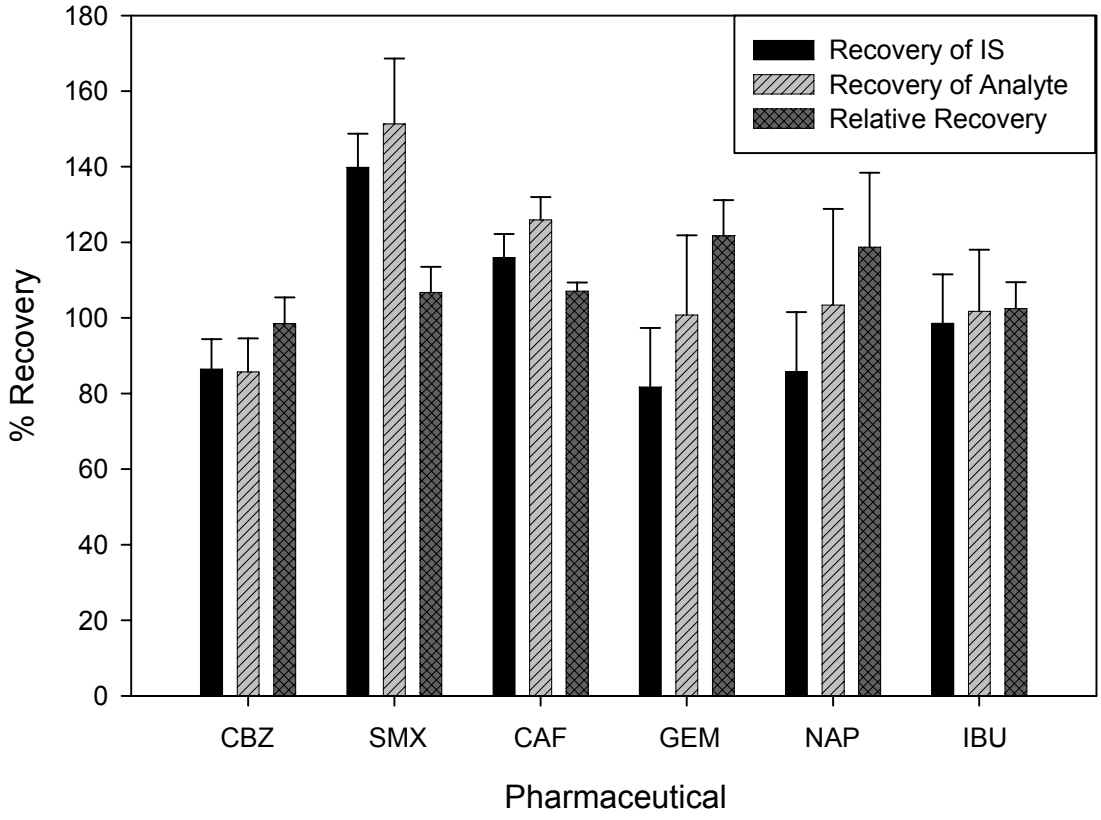


Figure 2. 3 – Absolute method recovery for analytes and internal standards (IS) for carbamazepine (CBZ), sulfamethoxazole (SMX), caffeine (CAF), gemfibrozil (GEM), naproxen (NAP), and ibuprofen (IBU) is plotted. Recoveries were calculated by comparing the peak area of each analyte or IS in a set of method standards, to the peak area found in the calibration standards. The relative recovery, which considers the ratio of the analyte to that of the internal standard, is also provided, and illustrates the degree to which the use of isotope dilution techniques help to correct poor recoveries. Standard deviations are plotted for a sample size of 4.

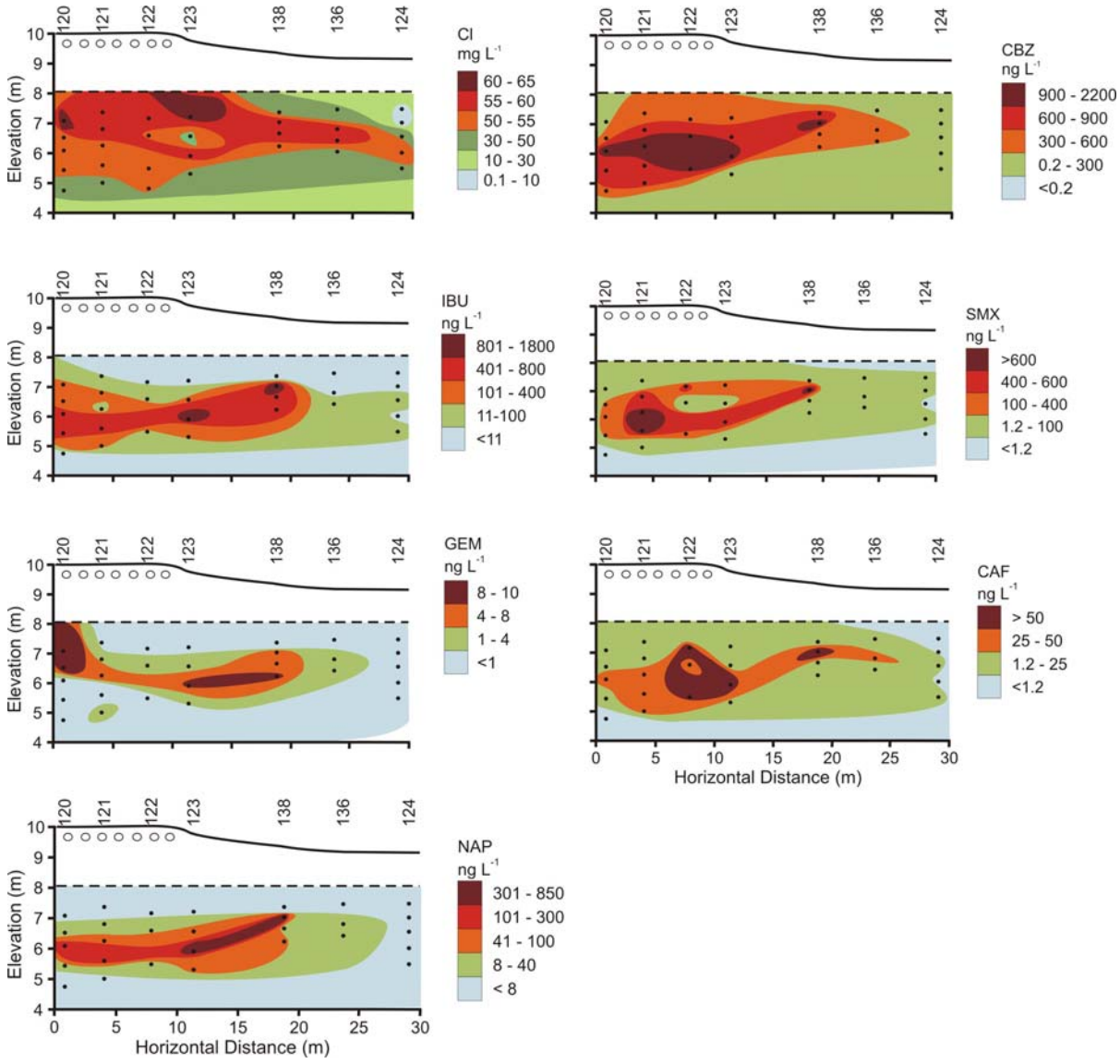


Figure 2. 4 - Groundwater plumes downgradient of the Long Point septic tile bed for the pharmaceuticals of interest; carbamazepine (CBZ), ibuprofen (IBU), sulfamethoxazole (SMX), naproxen (NAP), caffeine (CAF), and gemfibrozil (GEM), as well as the conservative tracer (Cl).

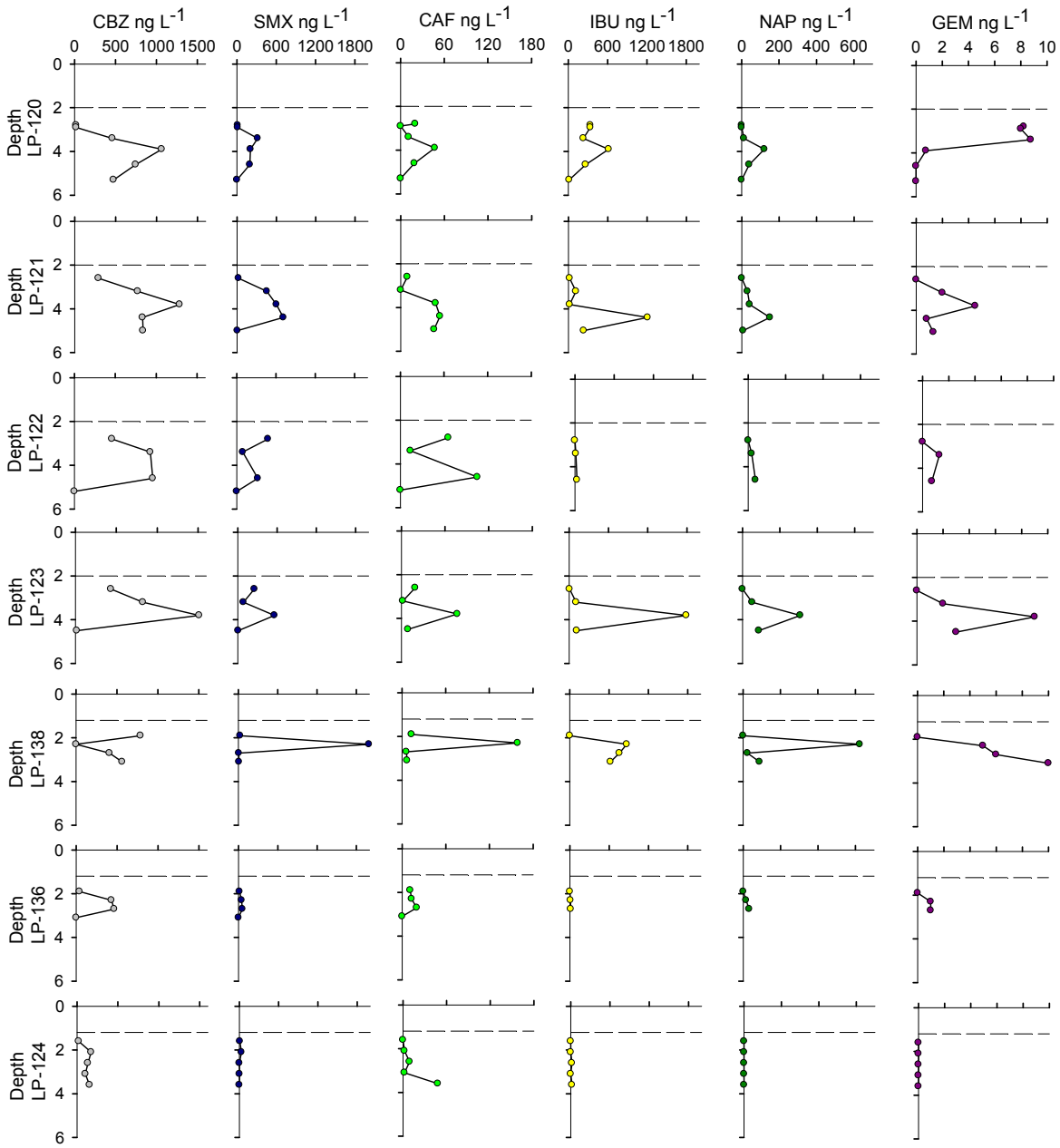


Figure 2. 5 – Depth (m) profiles for pharmaceutical compounds of interest carbamazepine (CBZ), sulfamethoxazole (SMX), caffeine (CAF), ibuprofen (IBU), naproxen (NAP) and gemfibrozil (GEM) at sampling points downgradient of the Long Point septic bed.

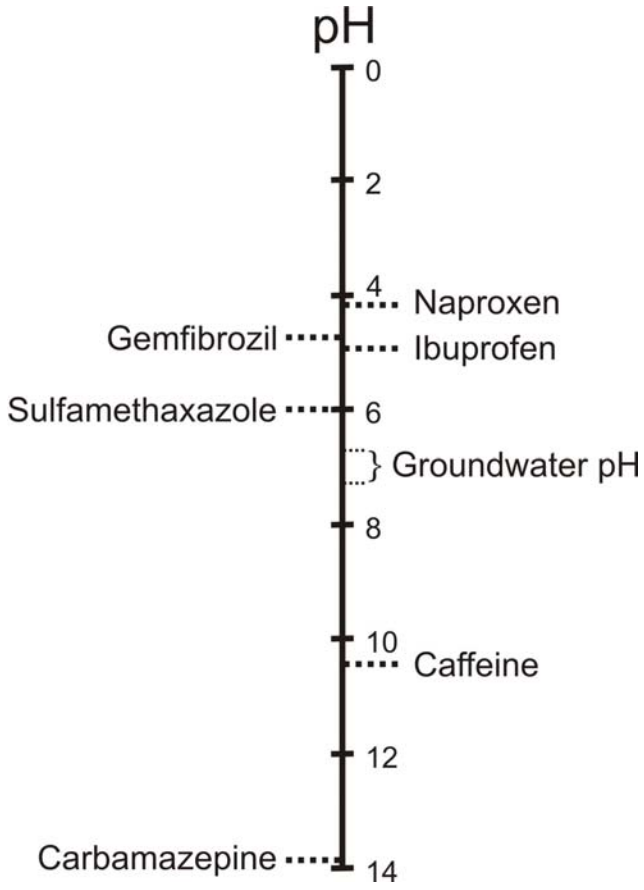


Figure 2. 6 – pK_a of each pharmaceutical of interest plotted on the pH scale. The pH range of groundwater in the Long Point aquifer is noted (6.7 – 7.2) as obtained from Carrara et al. (2008)

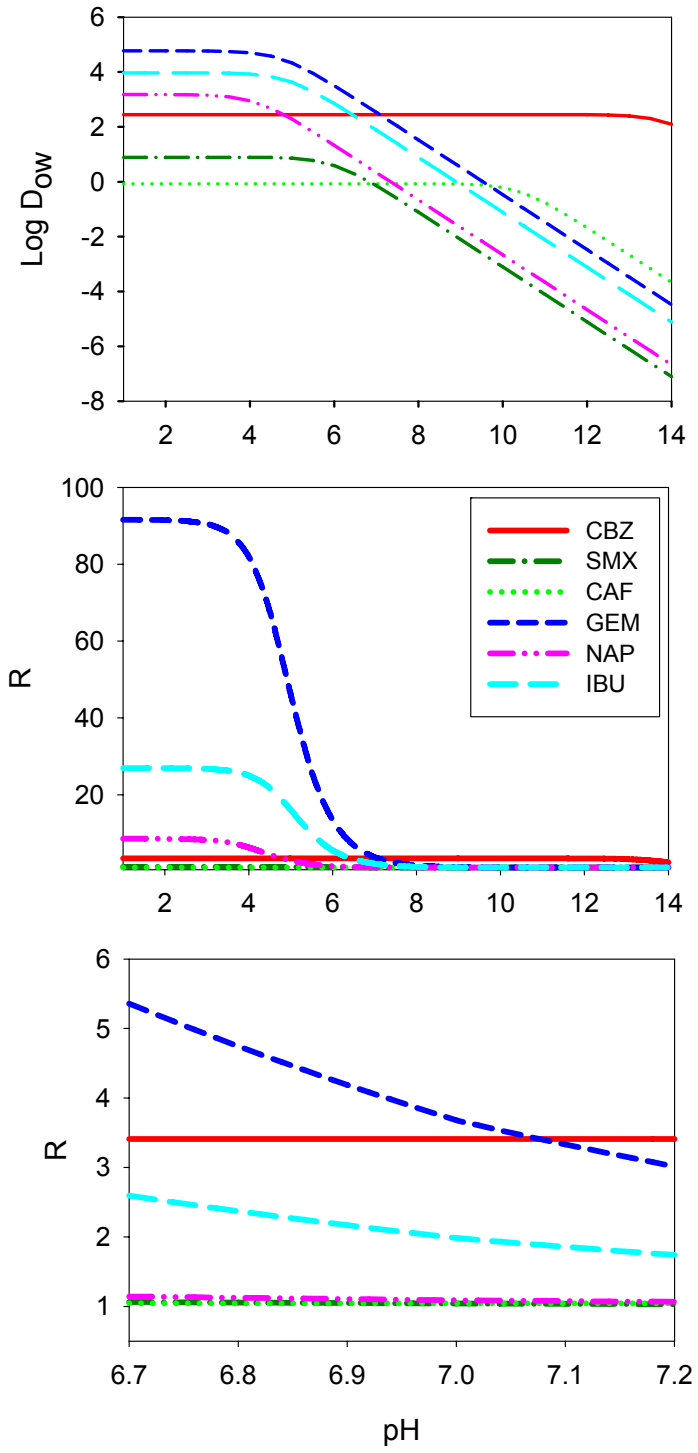


Figure 2. 7 – Log D_{ow} calculated for each pharmaceutical of interest calculated across the entire pH range. The pH range at the Long Point Septic site is between 6.7 and 7.2 (Carrara et al., 2008). Retardation coefficients (R) calculated using the D_{ow} values, presented over the entire pH range, as well as the pH range observed at the Long Point septic site by Carrara et al. (2008).

3.0 Characterization of Municipal Landfill Leachate Plumes and the Search for Pharmaceuticals

3.1 Introduction

Municipal landfill waste disposal sites have been identified as sources of contamination to groundwater. Some of the more common contaminants include dissolved organic carbon (DOC), NH_4, benzene, toluene, and aromatic hydrocarbons (Christensen et al., 2001). However, specific contaminants observed in leachate plumes vary from site to site depending on the type of waste deposited, the control measures in place, and the site hydrogeology and geochemistry.

The properties of leachate are determined by the type of waste deposited (Christensen et al., 2001). This leachate will migrate downward through the base of the landfill if a leachate collection system or leachate liner is not 100% effective, or in the case of older landfills, if there are no leachate control measures in place. After leachate leaves the waste pile, it often infiltrates through the unsaturated zone, eventually forming a plume of groundwater contamination. The transport of this plume is strongly controlled by the geochemical properties of the site, including pH and oxidation-reduction conditions (Christensen et al., 2001; Bjerg et al., 2005).

3.1.1 Waste Disposal Patterns

Disposal patterns of unused or expired medications appear to be dependant on the habits of the patient, the type of drug, and the rate of prescription and drug consumption (Bound and Voulvoulis, 2005). Bound et al. (2006) observed that for a U.K. sample population of 400 households, 63.2 % of people surveyed had disposed their drugs in the municipal waste

stream, and 11.5 % had deposited them into their household grey or black water. A follow-up study conducted by Slack et al. (2007b) in the U.K. found that from a survey of 500 homes, 55.8 % of survey participants had disposed of their drugs into the municipal waste stream, while only 9.9 % had disposed of drugs down the drain. From this information, it was estimated that 280 T of medicinal waste enters municipal landfills each year in the UK. In the U.S., new federal guidelines have been issued to minimize disposal of pharmaceutical waste down the drain, instead favouring disposal in municipal waste streams (Halford, 2008), potentially resulting in an increase in the proportion of pharmaceutically active compounds (PhACs) that are landfilled. In addition to disposal of unused or expired drugs, human or veterinary drugs may also be present in the municipal waste stream as a result of the disposal of human and pet feces and urine. Overall, there is evidence that PhACs are being deposited into municipal waste streams, and will likely continue to be a part of household waste into the future.

3.1.2 Pharmaceuticals in Groundwater

The presence of PhACs has been studied in groundwater and surface water with possible sources being identified in Figure 1.1. The study of pharmaceuticals in groundwater has received less attention than pharmaceuticals in surface water, but in recent years, the number of studies documenting the presence of pharmaceuticals in groundwater has been increasing. Some of the identified sources to groundwater include bank infiltration (Kreuzinger et al., 2004; Massmann et al., 2008), artificial groundwater recharge (Drewes et al., 2002), agricultural infiltration (Heberer et al., 1998; Scheytt et al., 2007; Siemens et al., 2008), septic systems (Conn et al., 2006; Swartz et al., 2006; Godfrey et al., 2007; Carrara et al.,

2008), leaky sewer systems (Fenz et al., 2005) and landfills (Eckel et al., 1993; Schwarzbauer et al., 2002; Holm et al., 1995).

Godfrey et al. (2007) observed pharmaceuticals including carbamazepine and sulfamethoxazole at concentrations up to 450 ng L^{-1} in a shallow aquifer below a high school septic bed in Montana. The same study also detected pharmaceuticals in groundwater below an urban area containing multiple residential tile beds at concentrations less than 25 ng L^{-1}, with the exception of caffeine that was found to have a maximum concentration of 206 ng L^{-1} (Godfrey et al., 2007). Carrara et al. (2008) found evidence that septic beds can act as sources of PhACs to groundwater. An evaluation of groundwater downgradient of a tile bed in Long Point, Ontario detected the presence of several pharmaceutical compounds having maximum concentrations in the range of 20 to 12,000 ng L^{-1}. Siemens et al. (2008) observed a variety of drugs including ibuprofen and naproxen in shallow groundwater below an irrigation field. Caffeine was detected in groundwater in a variety of settings, including below an agricultural field irrigated with sewage effluent (40 ng L^{-1}) and in a monitoring well below an urban subdivision contaminated with domestic waste water (230 ng L^{-1}), where caffeine was also detected (Seiler et al., 1999). Carbamazepine was found entering groundwater through leaky sewage systems, resulting in a maximum average groundwater concentration of 30 ng L^{-1} (Fenz et al., 2005). Carbamazepine was also observed in groundwater being infiltrated with sewage effluent, suggesting that it was resistant to attenuation in the unsaturated zone (Seiler et al., 1999; Kreuzinger et al., 2004). Ibuprofen and carbamazepine were detected in groundwater as a result of groundwater recharge (Drewes et al., 2003). Groundwater below two golf courses irrigated with treated wastewater

had detectable amounts of carbamazepine and caffeine, and sulfamethoxazole, ibuprofen, gemfibrozil and carbamazepine were found in groundwater at the ng L^{-1} range below a receiving and holding pond for treated wastewater (Snyder et al., 2004). Therefore, a variety of field studies have detected measurable concentrations of various pharmaceutical compounds in groundwater settings, identifying a variety of different sources, and the ability of PhACs to be present and persist in groundwater environments.

3.1.3 Pharmaceuticals in Landfills

The potential contamination of groundwater as the result of pharmaceutical disposal in sanitary landfills has been postulated by a number of investigators (Heberer, 2002; Bound and Voulvoulis, 2005; Doerr-MacEwan and Haight, 2006; Seeusen and Edwards, 2006; Nikolaou et al., 2007), however, there are limited studies documenting pharmaceutical occurrence in leachate plumes. One of the first studies to find the presence of a pharmaceutical compound downgradient of a landfill qualitatively identified three compounds at concentrations up to 1 μg L^{-1} at a single well 300 m away from the landfill in a shallow sandy aquifer (Eckel et al., 1993). This study indicated the potential for landfills to leach pharmaceuticals into groundwater, and therefore identified the need for further studies. Holm et al. (1995) looked for the presence of pharmaceuticals downgradient of a landfill used for waste disposal from the pharmaceutical industry. Close to the landfill, sulfonamides reached concentrations upwards of 6,470 μg L^{-1}. All drugs detected appeared to become fully attenuated and were non-detectable 150 m away from the landfill. A screening for several pharmaceuticals was performed at a landfill that had high rates of seepage into groundwater due to minimal bottom sealing (Schwarzbauer et al., 2002). The leachate

entered a former mining system consisting of shafts and tunnels situated below the waste pile. Ibuprofen, clofibric acid and propylphenazone were detected in all samples collected at concentrations as high as 140 μg L^{-1}. More recently, Ahel et al. (2004) observed PhACs in landfill leachate and groundwater samples at a municipal landfill accepting industrial waste. The PhACs were intermediates developed from the synthesis of vitamin C. A study conducted by Barnes et al. (2004) discovered PhACs including triclosan in relatively shallow wells downgradient of an old, unlined municipal landfill. Overall, information on the fate of PhACs in properly engineered municipal landfills or landfills that are not accepting wastes from the pharmaceutical industry appears limited.

3.1.4 Purpose of Study

Based on the volumes used, the disposal patterns, and the biologically active nature of pharmaceuticals, it is important to investigate the possibility of pharmaceuticals emanating from landfills in groundwater plumes. The current literature reflects a bias towards research on wastewater treatment plants as sources, rather than landfill leachate (Bound and Voulvoulis, 2005), and therefore the risks of pharmaceuticals to the environment may not be fully understood. This current study was conducted in an attempt to overcome the apparent gap in research by investigating the possibility that engineered municipal landfills can act as sources of pharmaceuticals to groundwater.

3.2 Methods

3.2.1 Site Descriptions

The Cambridge landfill is located within Cambridge, Ontario, Canada. The site is 123 hectares, of which 38 are licensed for non-hazardous waste disposal. The landfill accepted primarily domestic waste, as well as some commercial and industrial waste from the time it opened in 1973, to when it closed and was capped in 2003. Upon closure the landfill had reached a final capacity of 2,650,000 tonnes of waste. Initially constructed without a leachate containment system, it was gradually upgraded to meet design requirements. It is a geologically complex site, with strata from surface downward being: silts and sands, clayey silts/sands, sand/silty sand till, sand and gravel, and bedrock. The clayey silt layer is not continuous throughout the site, but where present acts as a confining layer and allows for the presence of a shallow perched aquifer. The regional aquifer, and the one which nearby municipal supply wells draw their water from, is located within the deep sand and gravel unit, with the water table being approximately 20 m below the base of the waste pile. Groundwater flow in the regional aquifer is generally towards the west, however, containment pumping wells have influenced parts of the local groundwater flow direction (CH2MHILL, 2008)

The Waterloo landfill is located in Waterloo, Ontario, Canada. The original landfill was in operation from 1972-2002, and currently an expansion cell directly north of the original landfill is being filled, with additional expansion cells being constructed. In 2007, the year in which sampling occurred, 244,000 tonnes of refuse was accepted at the site. The base of the original landfill is 0.25 km^2 in area, and the height of the waste pile is up to 30 m. The water

table is located 30 m below the base of the pile. Directly below the surface, there is an upper fine-grained till unit extending from 1 m to 30 m deep. Previously, a detailed network of monitoring wells was installed around the landfill, throughout the property, and on other properties downgradient and upgradient of the landfill. Groundwater flow is from west to east below the landfill (Region of Waterloo, 2008).

3.2.2 Field Methods

The sampling at the Cambridge Landfill was conducted in June 2007. A total of 31 wells were sampled (Figure 3.1), each located within an associated leachate plume. Thirteen of these wells were located within a plume extending to the northwest of the site along transect C-C'. The wells sampled contained concentrations of vinyl chloride, 1,1-DCA, and benzene, and were also selected due to their relative proximity to a municipal drinking water supply well. The remaining 18 wells were selected based on the presence of a leachate plume flowing to the southwest along transect D-D'. The wells sampled were selected based on concentrations of benzene, vinyl chloride, 1,1-DCA and chloride. Several of the wells sampled within this area were influenced by a pumping containment system. A total of 4 leachate wells located directly in the refuse were sampled. The remaining wells were all considered groundwater wells and were outside the limit of refuse.

Sampling at the Waterloo Landfill was conducted during July, 2007. Twenty-three wells were selected for sampling. Of these, 19 were located along transect A-A' (Figure 3.2), which runs along the northeast side of the original landfill and extends approximately 600 m downgradient of the edge of the pile. The other four sampling points were located in the

west corner of the landfill, and were selected based on locations where high concentrations of vinyl chloride were observed, indicative of contamination derived from the landfill.

Samples were collected from piezometers with dedicated polyethylene tubing using a Waterra pump powered by a portable gasoline generator. At the Waterloo Landfill, some of the wells sampled were groundwater extraction wells, and as a result are continually purged and were sampled directly from a pre-configured tap. Samples were collected for PO_4-P, CH_4, pharmaceuticals, metals, DOC, NH_3/NH_4-N, and anions. All samples were filtered in the field using high capacity Wattera 0.45 μm filters. They were collected in HDPE Nalgene bottles, with the exception of the pharmaceutical samples, which were collected in amber glass bottles to prevent photodegradation and sorption to plastics, and the methane samples, which were collected in 20 mL septum-capped glass vials. Methane samples were collected by hand pumping the well to fill the polyethylene tube, then gently pouring the water into the vial to reduce introduction of air into the sample. Samples for analysis of pharmaceuticals, NH_3/NH_4-N, and PO_4-P were preserved in the field by acidifying to a pH < 2 using 16N H_2SO_4. Metals samples were preserved to a pH < 2 using 6N HNO_3. At each well, pH test strips were used to verify that the proper pH was achieved during the acidification process.

Groundwater temperature, pH, Eh, alkalinity, and dissolved oxygen (DO) (Waterloo Landfill only) were measured directly in the field using standard procedures. Alkalinity measurements were performed in the field using a Hach digital titrator. Filtered samples were titrated with 1.6 N H_2SO_4, using bromocresol green-methyl red indicator. A digital thermometer was used to determine the temperature of the groundwater. Measurements of

Eh and pH were made in a sealed flow-through cell using the slowest flow rate possible with the Wattera pump. The water for these measurements was unfiltered, with the exception of wells with particularly turbid water. The temperature of the flow through cell was maintained near groundwater temperatures through the use of an ice bath. An Orion Thermo Sure-Flow combination redox electrode and an Orion Thermo Ross combination electrode were used to measure Eh and pH. The electrodes were calibrated prior to sampling at each well using Zobell's and Light's solutions for the Eh electrode, and standard buffer solutions of pH 4 and 7, and checked against a pH 10 buffer for the pH electrode. Values for DO were approximated through the use of CHEMets® kits. At each field site, approximately 1 blind field duplicate was obtained for every 10 wells sampled, and multiple field blanks were collected.

3.2.3 Reagents

Drug standards for carbamazepine, gemfibrozil, naproxen, sulfamethoxazole, ibuprofen and caffeine were obtained from Sigma Aldrich Canada. For each analyte, a unique internal standard was used that was the same compound, with only a slight difference in properties due to a small change in the mass number as a result of it being labeled with an isotope. Table 2.1 outlines the unique internal standards used for each analyte, together with the properties of each analyte and internal standard. All internal standards were obtained from CDN Isotopes (Quebec, Canada) with the exception of sulfamethoxazole d_4 (Toronto Research Chemicals, Toronto, ON, Canada).

Nanopure water (Milli-Q water) was provided through the use of a 0.45 μm Millipore Q-Gard1 unit. High performance liquid chromatography (HPLC) grade methanol (MeOH) (99.9%), ammonium acetate, formic acid, acetic acid and acetonitrile were obtained from Caledon Laboratories Ltd. (Georgetown, ON, Canada).

All pharmaceutical stock solutions were prepared by measuring 10 mg of either an analyte or an internal standard and dissolving in MeOH/Milli-Q water (50:50 v/v), with the exception of gemfibrozil and its internal standard (gemfibrozil d_6), which were dissolved in 10% 0.03M NaOH in MeOH/nanopure water (50:50 v/v), and internal standards for ibuprofen and naproxen, which were dissolved in pure MeOH. The solvent selected was based on the solubility properties of each pharmaceutical.

3.2.4 Sample Preparation

Samples stored at 4°C were allowed to reach room temperature. Frozen samples were allowed to thaw to room temperature, and were vacuum filtered using 0.45 μm nylon filters to prevent clogging of the solid phase extraction (SPE) cartridges by a gel residue that formed as a result of freezing. A sorption study was conducted that evaluated the loss of the analytes onto the nylon filters. The results indicated that there was minimal to no sorption of all pharmaceuticals to the nylon filters (Hebig, 2008) and therefore it is not expected that this step will have affected the aqueous concentrations of the PhACs of interest. A laboratory blank was also prepared for each set of samples analysed.

One hundred mL of each sample was spiked prior to SPE with a mixture containing all six internal standards to achieve a concentration of 1 μg L^{-1} of each internal standard after the SPE step. Unique internal standards were utilized for each analyte to account for analyte losses during the SPE step and matrix suppression during analysis. Utilizing a unique internal standard for each pharmaceutical provides the most accurate representation of the unknown analyte to correct for losses during SPE, instrument suppression and other errors during analysis (Gros et al., 2007).

Solid phase extraction was performed using Oasis HLB 5 mL glass cartridges under approximately 13 cm (5 in.) Hg of vacuum. These cartridges have been used previously with success for PhAC analysis in environmental applications (Hao et al., 2006; Vanderford and Snyder, 2006; Feitosa-Felizzola et al., 2007; Gros et al., 2007; Díaz-Cruz et al., 2008). Cartridges were conditioned with 3 mL of HPLC grade MeOH and equilibrated with 3 mL Milli-Q water. The cartridges were loaded with the samples and washed using 3 mL of 5% MeOH (v/v). Finally, the cartridges were eluted with three repeats of 2 mL of MeOH. The eluate was collected in a glass amber bottle and stored at 4°C until time of analysis. Use of SPE cartridges serves two purposes, 1) impurities are removed from the samples to minimize instrument contamination and interferences during analysis, and; 2) the samples are concentrated to improve detection limits. In this study, 100 mL of sample was concentrated to 6 mL, yielding a concentration factor of approximately 17. A set of blind spiked laboratory samples were prepared with analyte concentrations of 0.1 μg L^{-1}, 0.5 μg L^{-1}, and 1.0 μg L^{-1}. The purpose of these spiked samples was two-fold, first to evaluate the analysis

and calibration of the MS/MS method, and secondly to evaluate the recovery of analytes and surrogate internal standards passing through the SPE cartridges.

Samples that were frozen were extracted within 10 months, and all samples extracted in MeOH were analyzed within 6 months. A series of extractions on duplicate samples were performed over the 10 month period, with good reproducibility between separate analyses. In addition, results were reproducible between identical samples reanalyzed after being stored in MeOH between 0 to 6 months.

3.2.5 Pharmaceutical Analytical Methods

Analysis for pharmaceutical compounds was performed using high performance liquid chromatography electrospray tandem mass spectrometry (HPLC-ESI-MS/MS). The HPLC was an Agilent 1100 series operated using an eluant gradient. The mass spectrometer was an Applied Biosystems MDS SCIEX 4000QTrap. The nebulizer gas at the ionization source and the collision gas used to fragment the parent ion was N_2. A multiple reaction monitoring scan (MRM) was utilized for quantification, which occurred through a signal ratio between the analyte peak to that of the corresponding internal standard.

The analytical procedures utilized were modified from procedures described by Vanderford et al. (2003) and Stafiej et al. (2007). Analyses of caffeine, carbamazepine and sulfamethoxazole were conducted in positive ESI mode. A Symmetry RP18 column (Waters Corporation, Mississauga, ON, Canada) was used with a length of 50 mm, an internal diameter of 4.6 mm, and a particle size of 3 μm. The flow through the column was 1.25 mL

min^{-1}, with an injection volume of 15 μL. Mobile phase A consisted of 5 mM ammonium acetate and 0.1 % formic acid in nanopure water. Mobile phase B was 100 % MeOH with 0.1 % formic acid. The gradient started at 15 % for mobile phase B, after 0.76 min increased to 100 %, then at 2.5 min decreased back to 15 % until 4 min was reached.

Naproxen, gemfibrozil, and ibuprofen were analysed in negative ESI mode. An XDB-C18 column (Agilent Technologies, Mississauga, ON, Canada) with a length of 150 mm, an internal diameter of 4.6 mm and a particle size of 5 μm was used. The flow rate through the column was 1 mL min^{-1}, with a total injection volume of 10 μL. Mobile phase A, at pH 4, was 30 % acetonitrile diluted with nanopure water with 6.9 mM acetic acid. Mobile phase B was 100 % acetonitrile. The gradient started at 0 % of mobile phase B, at 18 min increased to 3 %, at 22 min to 12%, 40 min to 40 %, and ended at 45 min at 0 %.

3.2.6 Calibration

Instrument calibration was performed using an 8-point linear regression and a weighting factor of $1/x^2$, with a linear correlation coefficient of at least 0.999 (Table 3.1). The accuracies of most calibrations standards used were 100 +/- 5% (Table 3.1). Accuracy is a measure of how close the calculated (measured) value was for each calibration standard, to the expected concentration. The method detection limit (MDL) and limit of quantification (LOQ) were determined using a signal-to-noise ratio with a standard deviation of 3, where a signal to noise ratio of 3 was used to calculate the MDL and 10 was used to calculate the LOQ. Instrument detection limits are provided in Table 3.1, together with method detection limits that are corrected for the SPE concentration factor. The concentrations were calculated

using the external calibration curve, which were then corrected using the measured responses for the internal standards added to each sample.

3.2.7 Geochemical Analytical Methods

Methane samples were analyzed within 7 days of collection using head-space analysis gas chromatography with a flame-ionization detector (GC/FID) and a method modified from Blicher-Mathiesen et al. (1998). Determinations of ammonia concentrations were made using automated colorimetric procedures at an external laboratory. Phosphate determination was done spectrophotometrically with a HACH DR/2010 at 880 nm using the HACH ascorbic acid - molybdenum blue method. Anion concentrations were performed using ion chromatography. For the Cambridge Landfill, blind duplicates for all geochemical parameters were consistent, with the average percent difference being 3.3 %. In addition, the field blank was below method detection limits for all geochemical parameters with the exception of Cl and SO_4, which had measurable concentrations. The Waterloo Landfill duplicate analyses were also consistent, with an average percent different for all geochemical parameters being 10.5 %.

3.3 Results and Discussion

3.3.1 Geochemical Setting

Results of chemical analyses at the Cambridge landfill site were plotted along two cross sections. The first cross section (C-C'), extends approximately 400 m, and begins with a well drilled directly through the refuse at the top of the waste pile. Several parameters (Eh, alkalinity, anions) were not analyzed for the leachate wells due to the high organic content of

the samples. Figure 3.3 illustrates the geochemistry at the site (Appendix D). The pH and Eh values generally were lowest close to the landfill (6.45 and 18 mV, respectively), increasing in value downgradient from the landfill. The pH was acidic to neutral close to the landfill, and became more basic in a downgradient direction. Concentrations of alkalinity, Cl, CH_4, DOC, NH_3/NH_4-N all decreased with an increase in distance from the landfill. Maximum concentrations were 1,624 mg L^{-1} as $CaCO_3$ (alkalinity), 508 mg L^{-1} (Cl), 10.5 mg L^{-1} (CH_4), 65.4 mg L^{-1} (DOC), 46.6 mg L^{-1} (NH_3/NH_4-N). NO_3 was not observed in measurable concentrations (<0.4 mg L^{-1}) at any sampling location, whereas SO_4 only appeared at elevated concentrations 150 m downgradient from the landfill (up to 792.6 mg L^{-1}). Concentrations for PO_4-P were very low across the entire cross sections, with a maximum concentration of 0.08 mg L^{-1}.

The second cross section (D-D') sampled at the Cambridge Landfill extends approximately 800 m, and begins with a well drilled directly through the refuse at the top of the waste pile, and ends approximately 500 m past the limit of refuse. No distinct trend was observed for pH, with values ranging from 6.47 to 7.79 along the plume. In general, Eh measurements were lowest in the deepest wells and closer to the landfill; and further downgradient from the landfill, values increased.

Concentrations were generally low close to the water table, particularly for Cl, possibly indicating that some of the wells sampled closest to the landfill were located on the fringe of the plume and not necessarily indicative of the plume core. Leachate plumes are typically narrow (Christensen et al., 2001), further suggesting that this is the case. In addition, Eh and

alkalinity were not measured in the three leachate wells sampled along this cross section. The concentration distributions are illustrated in Figure 3.4. DOC, alkalinity, Cl, CH_4, NH_3/NH_4-N, and PO_4-P were generally found to have higher concentrations in the wells closest to the landfill, and decreased away from the landfill due to redox processes such as nitrification and oxidation of organic matter, and/or mechanical dispersion. Maximum concentrations for these parameters were 881 mg L^{-1} (DOC), 1,052 mg L^{-1} as $CaCO_3$ (alkalinity), 652.3 mg L^{-1} (Cl), 17 mg L^{-1} (CH_4), 1,550 mg L^{-1} (NH_3/NH_4-N) and 1.72 mg L^{-1} (PO_4-P). NO_3-N was only detected at a single location approximately 200 m downgradient from the landfill (1.53 mg L^{-1}), likely as a result of oxidation of NH_3/NH_4-N, and SO_4 concentrations tended to be highest 200 m downgradient, with a maximum measured concentration of 58.7 mg L^{-1}. These trends are consistent with redox processes occurring in the denitrification zone, where the oxidized species SO_4 and NO_3-N would typically be observed downgradient from the landfill (Bjerg et al., 2005).

At the Waterloo landfill, geochemical analyses (Appendix E) were determined for a single cross section (A-A') (Figure 3.5) and are presented in Figure 3.6. In this cross section, many of the wells extended along the edge of the landfill, but were not located directly below the waste pile and are therefore considered groundwater wells and not leachate wells. Wells sampled extend approximately 800 m downgradient from the limit of refuse. In general, pH and Eh were found to be lowest closer to the landfill (6.1 and 37 mV, respectively), and increased further downgradient and with greater depth below the waste pile. Similar to the Cambridge site, values for alkalinity (760 mg L^{-1} as $CaCO_3$), Cl (58.34 mg L^{-1}), CH_4 (19.5 mg L^{-1}), PO_4-P (0.027 mg L^{-1}) and DOC (55.3 mg L^{-1}) were highest closer to the landfill, and

decreased moving downgradient from the landfill. Sulfate was found in nearly all wells, however, the highest concentrations were found in wells located downgradient of the waste pile (67.7 mg L^{-1}). Concentrations of NO_3-Ns were observed below detection (0.4 mg L^{-1}) in all wells with the exception of two located approximately 500 m downgradient of the landfill, which is similar to findings across Cambridge cross section D-D' where NO_3 was only present in one well downgradient of the waste pile. NH_4/NH_3-N was only detected in one well near the waste pile (0.2 mg L^{-1}), with the remainder of the wells along the cross section being at or below detection (< 0.1 mg L^{-1}). Along this cross section, DO was also determined and it was found that concentrations were less than 3 mg L^{-1} for all wells sampled, however, DO tended to be higher closer to the water table.

The geochemistry of landfill leachate plumes extending into groundwater has been described widely in the literature (e.g., Christensen et al., 2001; Kjeldsen et al., 2002; Bjerg et al., 2005; Lee et al., 2006). The geochemical conditions observed at the Cambridge and Waterloo landfills were fairly consistent with leachate plumes emanating from engineered municipal landfills. Namely, the presence of reduced species close to the landfill with decreasing concentrations moving downgradient, coupled with the introduction of more oxidized species further from the landfill. The measured Eh also was observed to increase with distance at each landfill as the plume became more oxidizing. The geochemistry at each site being typical of municipal waste sites allows for useful application of the results with regards to pharmaceuticals at other landfills with similar designs, waste streams, geochemistry and geology.

3.3.2 Pharmaceuticals

3.3.2.1 QA/QC

Pharmaceutical analyses were conducted along the cross section for caffeine, carbamazepine, sulfamethoxazole, gemfibrozil, naproxen and ibuprofen. Concentrations of all drugs analysed were consistently below detection in laboratory and field Milli-Q blanks prepared using the same SPE process employed for the unknown samples (Table 3.2), with the possible exception of caffeine at concentrations less than 1 ng L^{-1}, suggesting contamination within the instrument. However, because the background peak for caffeine was present in all samples, including the calibration standards, no correction beyond those obtained through the application of the calibration regression equation was required. Blank MeOH/Milli-Q samples spiked with internal standards for direct injection into the HPLC were below detection limits (Table 3.1) for all analytes, indicating the purity of the internal standards used (Table 3.2).

Blind Milli-Q spiked samples prepared for quality control measures had high accuracies (91-110 %) for all drugs across a range of concentrations (100 to 1000 ng L^{-1}) (Table 3.2), indicating the accuracy of the calibration and analysis methods. The accuracy is calculated by comparing the measured concentration in the quality control samples, to the expected concentration.

3.3.2.2 Absolute Method Recovery

The absolute method recovery of the internal standards was expressed by comparing the peak area (counts) of the internal standard in a control set of Milli-Q spiked samples (method

standards) passed through the SPE cartridges (n = 4) to MeOH/Milli-Q calibration standards (calibration standards) prepared for direct injection into the HPLC (Equation 3.1).

$$\text{Absolute IS Method Recovery (\%)} = \frac{\text{IS Peak Area in Method Standards}}{\text{IS Peak Area in Calibration Standards}} \times 100 \qquad (3.1)$$

In all unknown samples as well as the method standards, the internal standards were added prior to SPE, therefore the absolute method recovery is representative of the recovery of the SPE process, as well as the instrument detection capabilities. The method standards were prepared to have final analyte concentrations of 0.2, 0.5, 1.0, and 5.0 μg L^{-1}. The effect of passing samples through a nylon filter is expected to be negligible for all of the drugs, based on a sorption study which indicated little to no loss of the PhACs from the aqueous phase when in continued contact with the nylon filters (Hebig, 2008).

In addition, the absolute analyte recovery was calculated (Equation 2.2) for the method standards using the same method of comparing peak area in the method standards to peak area in the calibration standards (Table 2.4, Figure 2.3).

$$\text{Absolute Analyte Method Recovery (\%)} = \frac{\text{Analyte Peak Area in Method Standards}}{\text{Analyte Peak Area in Calibration Standards}} \times 100 \qquad (3.2)$$

The relative recovery of the analyte to internal standard was also calculated through a series of equations (Equations 3.3 and 3.4) to help indicate the relation between internal standard recovery and calculated analyte concentration. The relative recovery ratio (Equation 3.3) was calculated for both the method standards and the calibration standards and then used to calculate the relative method recovery (Equation 3.4).

$$\text{Relative Recovery Ratio} = \frac{\text{Analyte Peak Area}}{\text{IS Peak Area}} \times 100 \qquad (3.3)$$

$$\text{Relative Method Recovery (\%)} = \frac{\text{Relative Recovery Ratio in Method Standards}}{\text{Relative Recovery Ratio in Calibration Standards}} \times 100 \qquad (3.4)$$

The relative recovery is more reflective of the accuracy of the calibration and method, as it considers not only the internal standard recovery, but also the analyte recovery and therefore accounts for the isotope dilution technique that was used to calculate the final concentration of analytes in all samples.

Table 2.4 and Figure 2.3 illustrate the three parameters calculated for the absolute method recovery of the method standards. It is noted that ibuprofen (99 %), naproxen (86 %) and carbamazepine (86 %) had the best absolute recoveries of internal standards, however, the precision for all drugs ranged between 6 and 16 %. Sulfamethoxazole had a very high internal standard absolute recovery (140 %), however, the absolute recovery of the sulfamethoxazole analyte was also high (151 %), which resulted in a satisfactory overall relative recovery of 107 % (Table 2.4, Figure 2.3), illustrating the importance and success of utilizing an appropriate internal standard for each individual analyte.

For most of the pharmaceuticals analysed, the absolute recovery of the internal standard in the method standards was similar to the absolute recovery of the corresponding analyte, which resulted in a desirable relative recovery. Carbamazepine, sulfamethoxazole, caffeine, and ibuprofen all had relative recoveries in the range of 99 to 107 %. Naproxen and gemfibrozil had higher relative recoveries (119 % and 122 % respectively), which indicates that measured values for these drugs could be elevated by approximately 20 % (Figure 2.3).

3.3.2.3 Internal Standard Recovery

Another recovery calculated took into consideration the matrix effects of each individual sample, combined with the absolute method recovery (Table 3.3). In this recovery, the peak area of the internal standard in all unknown samples was compared to the peak area of the internal standard in the calibration standards that were analysed together within a single group of samples (Equation 3.5).

$$\text{IS Recovery (\%)} = \frac{\text{IS Peak Area in Unknown Samples}}{\text{IS Peak Area in Calibration Standards}} \times 100 \qquad (3.5)$$

For drugs analysed in positive mode, it was found that for carbamazepine, average sample recovery was low (52 and 60 % for Cambridge and Waterloo respectively) with high % RSD (36 % and 17 %). Caffeine had a high sample recovery (128 % and 116 % respectively) and high % RSD (48 % and 25 %). Sulfamethoxazole had better average recoveries (95 % and 87 %), but still relatively high standard deviations. The high standard deviations are not unexpected, given that across each field site, the geochemical properties and matrix effects varied from location to location. Other studies investigating recoveries of pharmaceuticals in environmental samples found a wide range of recoveries and high standard deviations (Hao et al., 2006; Pedrouzo et al., 2007). In this study, it was observed that for samples with high DOC (> 2 mg L^{-1}), the recoveries were poor in comparison to the samples with low DOC (< 2 mg L^{-1}). Having organic carbon present in the samples may create a competition with the target compounds for the available binding sites on the SPE adsorbents. Alternatively, a previous study investigating surface waters did not find a correlation between DOC and recovery of analytes on SPE (Hao et al., 2006). Rather, they attributed low recoveries to reduced extractability and/or ionization efficiency resulting from interactions between DOC and target analytes in analysis. In particular, humic acids, a common component in landfill

leachates, were found to reduce signal suppression for some drugs (Hao et al., 2006). For sulfonamide drugs, humic acids were found to have no affect (Hao et al., 2006), which is a possible reason why average sulfamethoxazole recoveries were generally more satisfactory than caffeine or carbamazepine.

By dividing the sample locations at each field site into two separate populations defined by their DOC concentrations and focusing on the population with low DOC, in all cases the standard deviations were lowered, some quite dramatically, and average sample recoveries approached 100 % (with the exception of sulfamethoxazole) (Table 3.3). For blind spiked Milli-Q samples, recoveries of internal standards for positive drugs were also not ideal, however, relative recoveries indicated that the low internal standards recovery was compensated for in the final calculation of the analyte concentration due to isotope dilution techniques (Table 3.3). By selecting an internal standard that is similar to the analyte, the internal standards are expected to behave similarly to the analyte, and concentrations are accounted for by looking at the relative peak difference. Additionally, the use of unique internal standards provides confidence when samples have non-detectable amounts of the analyte, but the internal standard is present.

For the sample recovery of internal standards of the drugs analyzed in negative ESI mode, sample recoveries were closer to 100%, and standard deviations were lower for all drugs at each site (Table 3.3), indicating the method is perhaps more robust for these drugs. Dividing samples into two populations based on high and low DOC concentrations as was performed

for the positive drugs had minimal effect. It appears as though DOC had less affect on the recovery of the internal standards for the drugs analyzed in negative mode.

3.3.2.4 Pharmaceutical Findings

All samples collected were analyzed for the presence of pharmaceuticals with the exception of 77-89 (Waterloo Landfill) and CL 44B (Cambridge Landfill). All samples for both the Cambridge and Waterloo Landfills were found to be below detection limits (Table 3.1) for caffeine, carbamazepine, sulfamethoxazole, naproxen, gemfibrozil and ibuprofen. These negative findings were determined through the use of field, analytical and laboratory methods that have been successfully applied to a variety of other samples and sample matrices (Chapter 2; Siebert, 2007; Hebig, 2008), while employing high quality control measures. A variety of extractions on duplicate samples were performed at varying times between when the samples were initially collected, to the final extraction after storing frozen samples for up to 10 months. In all cases all PhACs were below detection, indicating good reproducibility between sample sets. In addition, calibration standards were repeatedly run over a period of hours and days, with continued high accuracy.

The lack of pharmaceuticals in groundwater goes not mean that organic contaminants are not present in the leachate plume, as vinyl chloride was detected during sampling events that occurred simultaneously to our sampling (Figures 3.3, 3.4 and 3.6) (Region of Waterloo, 2008; CH2MHILL, 2008).

3.3.2.5 Pharmaceuticals in Municipal Waste Streams

Previous studies conducted on surface water have found the presence of PhACs in the geographical area of interest in this study (Metcalfe et al., 2003; Hao et al., 2006; Lissemore et al., 2006; Lishman et al., 2006; Carrara et al., 2008). Carbamazepine was detected in concentrations averaging 16.2 ng L^{-1} in a large river at eight different sampling locations, one of which was classified as receiving urban input. In the same study, gemfibrozil (13.7 ng L^{-1}) and naproxen (41.7 ng L^{-1}) were found in surface water receiving urban waste (Hao et al., 2006; Lissemore et al., 2006). Another study conducted in southern Ontario also found the presence of pharmaceutical compounds including naproxen, gemfibrozil, and ibuprofen in groundwater below septic tile beds in concentrations ranging below detection to as high as 12,000 ng L^{-1} (ibuprofen) (Carrara et al., 2008), while a similar study found the six pharmaceuticals of interest downgradient of a tile bed in Southern Ontario (Chapter 2). Lishman et al. (2006) found the presence of multiple PhACs in Ontario municipal wastewater effluent, including gemfibrozil (mean 246 ng L^{-1}), naproxen (mean 452 ng L^{-1}), ibuprofen (mean 384 ng L^{-1}), while a similar study by Metcalfe et al. (2003) detected maximum concentrations of gemfibrozil (1.3 μg L^{-1}), naproxen (33.9 μg L^{-1}), ibuprofen (24.6 μg L^{-1}) and carbamazepine (2.3 μg L^{-1}) in sewage effluent across Canada. Therefore, it is well documented that many of the PhACs evaluated in this study are present in the local environment and used by the general population being serviced by the landfills. The only PhACs of interest without documentation of local environmental presence are caffeine and sulfamethoxazole. Caffeine is widely consumed in beverages and is a commonly held non-prescription medication, and sulfamethoxazole is an antibiotic that is typically used in high volumes (Khetan and Collins, 2007), therefore it is probable that these PhACs are utilized in

the geographical area of question. Based on studies on pharmaceutical disposal habits (Bound and Voulvoulis, 2005; Bound et al., 2006; Slack et al., 2007b), it is likely that some of these PhACs are being deposited into landfills through either direct disposal of unused or expired medications, or though the disposal of human (i.e. diapers) or pet feces and urine.

3.3.2.6 Municipal Waste Stream Characterization

The Cambridge and Waterloo landfills are classified as municipal landfills, and receive a mixture of domestic, industrial, commercial, and inert waste in proportions that are fairly typical of municipal landfills throughout Canada (Environment Canada, 1996; Biersteker, 2008). Several of the studies that found PhACs in landfill groundwater plumes were conducted at sites that had not received traditional municipal waste compositions. These sites received a relatively high amount of pharmaceutical waste from either the pharmaceutical industry or hospitals (Holm et al., 1995, Eckel et al., 1993). The difference in waste streams is a possible explanation for the presence of pharmaceutical compounds in these previous studies, contrasting with the lack of pharmaceuticals in groundwater presented herein.

3.3.2.7 Transport of Pharmaceuticals

Pharmaceuticals not being detected in three separate leachate plumes could be due to such low quantities being deposited that drugs are not found in detectable amounts, and/or the geochemical and geological conditions at each site are supportive of rapid attenuation, preventing pharmaceuticals from entering the groundwater in measurable concentrations. Holm et al. (1995) found that drugs present in groundwater downgradient of the landfill

seemed to degrade most in the strongly anaerobic zones, such as in the methanogenic, sulfate-reducing and iron-reducing zones. Because the landfills are strongly reducing, this could explain why the drugs were all below detection limits downgradient from the source, after passing through highly anaerobic areas.

In addition to the oxidation-reduction conditions at the site, the site configuration and geology could contribute to the lack of PhACs in the groundwater below and downgradient of the landfills. At each site studied, the leachate passes through an extensive vadose zone prior to entering the groundwater system. Previous studies have found that pharmaceuticals show higher degradation and lower mobility under unsaturated conditions than during saturated transport (Scheytt et al., 2006; Chapter 2). Many groundwater sites where elevated concentrations of pharmaceuticals have been identified, including two municipal landfills, have been characterized by shallow aquifer systems, with relatively thin vadose zones (Godfrey et al., 2007, Carrara et al., 2008, Ahel et al., 2004; Schwarzbauer et al., 2002). In addition, Barnes et al. (2004) found pharmaceuticals in groundwater downgradient of an unlined municipal landfill in an alluvial plain, suggesting the importance of a properly engineered landfill. Therefore, the conditions at the Cambridge and Waterloo landfills appear to be conducive to removal of any PhACs that may have been initially present in the leachate.

The presence and transport of these pharmaceutical compounds in groundwater is dependant on the individual properties of the PhACs themselves. Parameters such as the solubility, the acid-base dissociation constant (pK_a), and the log K_{ow} of each pharmaceutical affect their

transport. It can be assumed that the majority of pharmaceuticals in the landfill are deposited in the solid phase, therefore, the concentrations of PhACs found in the aqueous phase would be dependant on the solubility of each compound, as well as the degree of contact with the solid phase with leachate or percolating rainwater. The PhACs of interest with the highest solubilities are sulfamethoxazole and caffeine, with the remainder having moderately high solubilities (Table 2.1). Therefore, all of these drugs have the potential to be dissolved if in contact with an aqueous phase.

The pK_a and the log K_{ow} of each drug also plays an important role in their transport in groundwater. The pK_a denotes the pH at which each PhAC will dissociate (Figure 3.7). Given a measured pH range of 6.45 to 7.92 at the Cambridge landfill and 6.05 to 8.34 at the Waterloo landfill, all the acidic pharmaceuticals (ibuprofen, gemfibrozil, naproxen, sulfamethoxazole) would have been dissociated into their anionic forms in the groundwater. For all the pharmaceuticals studied, dissociation of the neutral parent compound would result in an anionic compound. The charge of each PhAC has implications on the degree of sorption to solid matter. It is difficult to predict the surface charge of the refuse within the waste pile, and how passage through the waste pile would affect sorption.

Perhaps most important are the processes that would occur directly in the landfill during waste decomposition. Several samples were collected at each field site from wells that were considered leachate wells, as they were within the limit of refuse. Based on the results from these wells and from typical waste pile geochemistry (Christensen et al., 2001), predication can be made regarding the possibility of elimination within the waste pile. A review of

literature found that pH in newer landfills ranges from 4.5 – 9 (Christensen et al., 2001), however, the pH at various locations within the waste pile will vary significantly depending on the age of the waste and the stage of decomposition. During the early stages of waste decomposition, the pH of the leachate is low, and as the landfill stabilizes and methanogenesis becomes a significant process, the pH increases (Christensen et al., 2001). This fluctuation in pH likely has implications on the fate and transport of PhACs. Initially when pH is low, not all compounds may be dissociated into their anionic forms, which could serve to hinder or enhance sorption affects. It is difficult to predict how sorption may be affected, given the complex nature of the matrix in the landfill and the inability to predict surface properties of any potential sorption sites. However, by examining parameters such as the pH dependant partitioning coefficient (log D_{ow}) and the retardation coefficients (R) over the typical pH range, and assuming that the lower pH is representative of the early stage of decomposition, several trends emerge. Log D_{ow} was previously described in Chapter 2, and is calculated by the following equation (Figure 3.8) (Stuer-Lauridsen et al., 2000):

$$D_{ow} = \frac{K_{ow}}{1+10^{pH-pK_a}} \tag{3.6}$$

The D_{ow} is important, particularly when assuming retardation coefficients. Calculating retardation within the waste pile requires a variety of assumptions, including a waste pile bulk density, porosity, fraction of organic carbon (f_{oc}), and the assumption of saturated conditions. The interpretation of retardation in this study is qualitative only, and as a result the final value of each retardation coefficient is not as important as the overall trends. Retardation was calculated by the following equation:

$$R = 1 + \frac{\rho_b}{n} K_d \tag{3.7}$$

An assumed bulk density (ρ_b) of 0.65 g cm^3, and an effective porosity (n) of 0.4 were used, which are representative of typical landfill waste properties (Slack et al., 2007a), with an assumed f_{oc} of 25%. The partitioning coefficient (K_d) was estimated from the following series of equations:

$$\log K_{oc} = 0.679 \log K_{ow} + 0.663 \tag{3.8}$$

as developed by Gerstl (1990) and recently employed by Löffler et al. (2005). However, in place of log K_{ow}, the log D_{ow} is used, allowing R to be calculated as a function of pH. The K_d is then estimated based on the generalized expression.

$$K_d = K_{oc} \ f_{oc} \tag{3.9}$$

The retardation for all the acidic drugs increased with decreasing pH within the pH range from 4.5 to 9 (Figure 3.8), particularly for ibuprofen and gemfibrozil which were the PhACs with the highest log K_{ow}. As a result, the retardation of the acidic PhACs is likely more pronounced during the initial acid phase of a waste pile, which could contribute to the lack of detection in groundwater. Considering the typically high organic fraction of waste, calculated retardation values were quite high, which could also contribute to attenuation of pharmaceutical compounds in landfill leachate plumes.

Therefore, when considering the absence of PhACs in the groundwater plumes at the Cambridge and Waterloo landfills, there are a variety of factors that must be considered, including the composition of the waste stream, the geochemistry and geology of the site, as well as the chemical properties of each PhAC. Further studies would be required to narrow the findings down to any one cause, and at this time it is believed that likely multiple factors are contributing to at least some degree to the elimination of PhACs in the leachate plumes.

3.3.2.8 Significance of Findings

The significance of the negative findings when investigating the presence of PhACs at two municipal landfills are two-fold. Firstly, prior to being able to definitively state that properly engineered, municipal landfills are not a consistent source of pharmaceuticals to groundwater, the need for additional studies has been identified. Future studies should focus on less detailed studies across a larger number of landfills and a larger suite of drugs. The second significant finding relates to public perception and government decision-making. A recent study conducted by Doerr-MacEwan and Haight (2006) investigated the opinions of 27 expert stakeholders in academia, industry and government on the presence of pharmaceuticals in the environment. Of these stakeholders, 81 % believed that pharmaceuticals compounds are a concern to ecosystem health, mostly due to the bioactive nature of drugs. As a result, it was generally believed (67 %) that it is somewhat or very important for government to take action to control the release of pharmaceuticals to the environment. If the findings of the study by Doerr-MacEwan and Haight are applied to the local government in the vicinity of these landfills, it is important to consider that for the pharmaceuticals evaluated, landfills were not a source to groundwater contamination. This finding has implications for government decisions related to where and how to implement control programs related to the release of pharmaceuticals to the environment to optimize both environmental controls and use of funds.

3.4 Conclusions and Recommendations

This study illustrates the possibility that 'typical' municipal landfills with modern and functioning control measures such as leachate collection systems and liners, coupled with a

typical municipal waste stream and characteristic plume geochemistry, may not be a consistent or definite contributor of pharmaceutical contamination to groundwater. The need for future studies has been identified, expanding the study to include a variety of landfills and performing a preliminary investigation of leachate collection systems to help to determine if the landfills are a consistent source of PhACs, and searching for an expanded suite of pharmaceuticals would also be recommended.

		Mode of Analysis	Range of Calibration (µg L^{-1}) Minimum 8 points	Linear Correlation Coefficient (r^2)	Range of Accuracy of Calibration Standards (%)	Instrument MDL/LOQ (ng L^{-1})	Method MDL/LOQ (ng L^{-1})
Carbamazepine		Positive				3/37	0.2/2.2
	Cambridge Landfill		0.1 - 20	0.9996	96 - 104		
	Waterloo Landfill		0.1 - 20	0.9998	97 - 102		
Sulfamethoxazole		Positive				23/78	1.4/4.6
	Cambridge Landfill		0.1 - 20	0.9997	96 - 103		
	Waterloo Landfill		0.1 - 20	0.9997	95 - 106		
Caffeine		Positive				0/20	0/1.2
	Cambridge Landfill		0.1 - 20	0.9998	97 - 102		
	Waterloo Landfill		0.1 - 20	0.9996	97 - 106		
Gemfibrozil		Negative	0.1 - 20	0.9995	95 - 107	15/65	0.9/4
	Cambridge Landfill						
	Waterloo Landfill						
Naproxen		Negative	0.1 - 20	0.9994	95 - 105	139/763	8/45
	Cambridge Landfill						
	Waterloo Landfill						
Ibuprofen		Negative	0.1 - 60	0.9994	92 - 109	189/648	11/38
	Cambridge Landfill						
	Waterloo Landfill						

Table 3.1 – Method Calibration. Calibrations were performed using an 8 point linear range with a $1/x^2$ weighting factor. The accuracy of the calibration standards illustrates how close the measured concentration of each standard was to the expected concentration. The instrument method detection limit (MDL) and limit of quantification (LOQ) is representative of the capabilities of the HPLC. The method MDL and LOQ is the instrument limit that has been corrected for the solid phase extraction (SPE) concentration factor.

		Accuracy of Blind Spikes (%) and %RSD	Blanks (Lab and Field, and blanks spiked with IS)
Carbamazepine	Cambridge Landfill	98 +/- 4	< 0.2 ng L^{-1}
	Waterloo Landfill	98 +/- 2	< 0.2 ng L^{-1}
Sulfamethoxazole	Cambridge Landfill	102 +/- 6	< 1.4 ng L^{-1}
	Waterloo Landfill	99 +/- 5	< 1.4 ng L^{-1}
Caffeine	Cambridge Landfill	98 +/- 2	trace peaks in blanks
	Waterloo Landfill	100 +/- 3	trace peaks in blanks
Gemfibrozil	Cambridge Landfill	121 +/- 2	< 0.9 ng L^{-1}
	Waterloo Landfill	105 +/- 4	< 0.9 ng L^{-1}
Naproxen	Cambridge Landfill	105 +/- 6	< 8 ng L^{-1}
	Waterloo Landfill	102 +/-6	< 8 ng L^{-1}
Ibuprofen	Cambridge Landfill	94 +/- 15	< 11 ng L^{-1}
	Waterloo Landfill	102 +/-4	< 11 ng L^{-1}

n = 3 (Cambridge)
n = 4 (Waterloo)

Table 3.2 – Quality Assurance and Quality Control. The accuracy of the blind spiked samples was measured by comparing the measured concentration to the expected concentration, and the residual standard deviation (%RSD) was also calculated. Blank samples were continually processed throughout each analytical run. Sample size (n) for each set of samples is noted.

		Sample Recovery of IS (%)	High DOC Sample IS Recovery (%)	Low DOC Sample IS Recovery (%)	Relative Recovery of Blind Spiked Controls (%)
Carbamazepine	Cambridge Landfill	52 +/- 36	32 +/- 53	62 +/- 14	98 +/- 2
	Waterloo Landfill	60 +/- 17	58 +/- 21	61 +/- 12	98 +/- 3
Sulfamethoxazole	Cambridge Landfill	95 +/- 24	107 +/- 24	88 +/- 21	104 +/- 6
	Waterloo Landfill	87 +/- 12	93 +/- 11	82 +/- 10	103 +/- 10
Caffeine	Cambridge Landfill	128 +/- 48	183 +/- 44	99 +/- 16	99 +/- 2
	Waterloo Landfill	116 +/- 25	133 +/- 26	101 +/- 8	101 +/- 2
Gemfibrozil	Cambridge Landfill	96 +/- 12	94 +/- 13	99 +/- 11	116 +/- 4
	Waterloo Landfill	99 +/- 9	97 +/- 10	100 +/- 8	102 +/- 4
Naproxen	Cambridge Landfill	92 +/- 18	87 +/- 20	97 +/- 17	105 +/- 10
	Waterloo Landfill	98 +/- 13	99 +/- 14	98 +/- 13	102 +/- 5
Ibuprofen	Cambridge Landfill	94 +/- 12	92 +/- 12	93 +/- 11	99 +/- 4
	Waterloo Landfill	101 +/- 10	101 +/- 12	101 +/- 8	106 +/- 13
		n = 38 (Cambridge) n = 31 (Waterloo)	n = 13 (Cambridge) n = 15 (Waterloo)	n = 25 (Cambridge) n = 16 (Waterloo)	n = 3

Table 3.3 – Recovery data. The recovery of each internal standard (IS) and the per cent relative standard deviation (%RSD) is noted for all samples. Recovery was determined by comparing the peak area of the internal standard in unknown samples, to the peak area of the internal standard in the calibration standards. For each pharmaceutical, the recovery was separated into two population based on DOC concentration; high (> 2 mg L^{-1}) and low (< 2 mg L^{-1}). In some cases, this DOC trend had an effect on the average and %RSD, where high DOC was associated with poor recovery. In addition, the relative recovery, which considers the ratio of the analyte to that of the IS is provided for the blind spiked samples. Samples size (n) is noted for each landfill site and for blind spiked control samples.

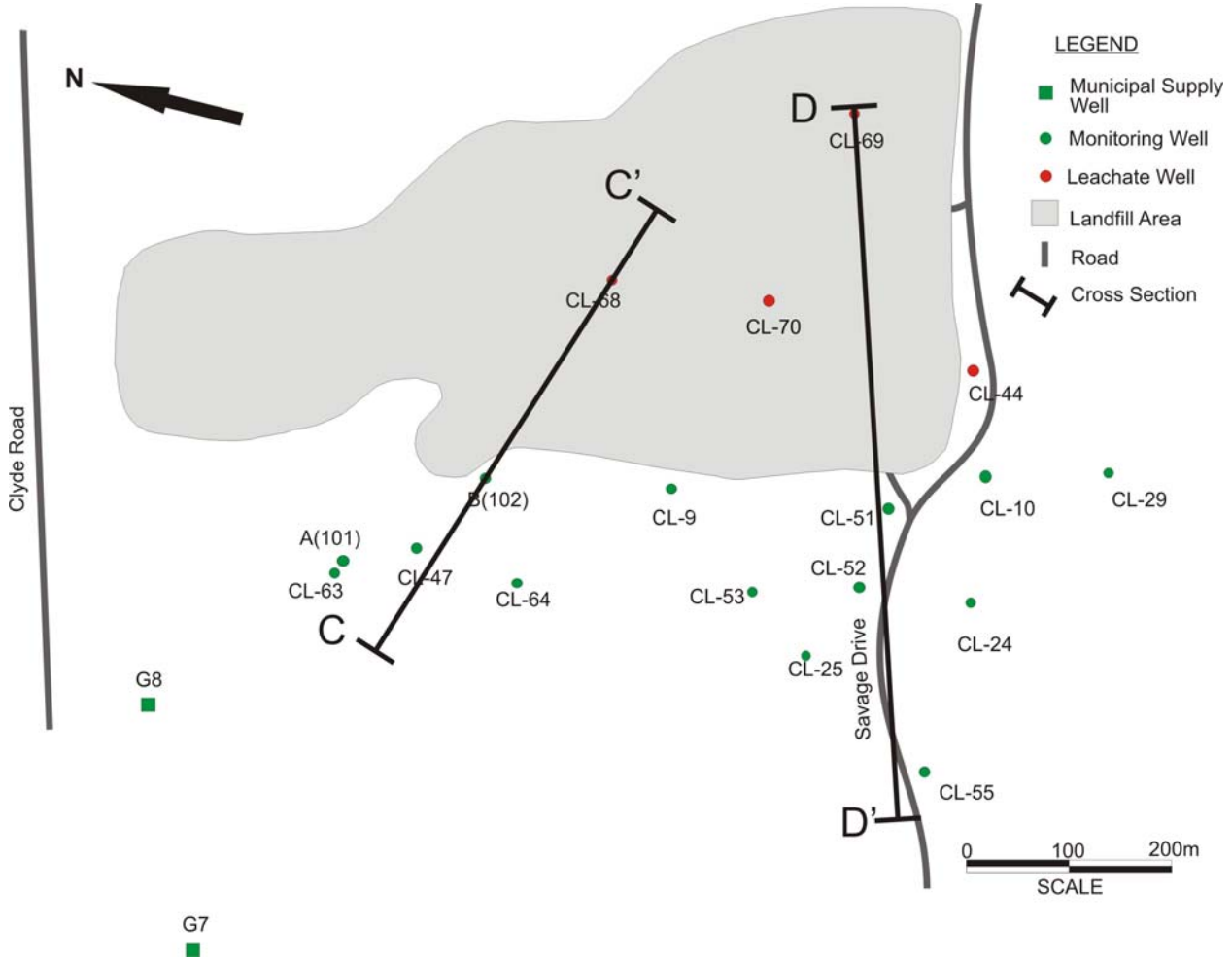


Figure 3.1 – Detailed plan view at the Cambridge Landfill. The location of all the sampling points are illustrated along cross sections C-C' and D-D'.

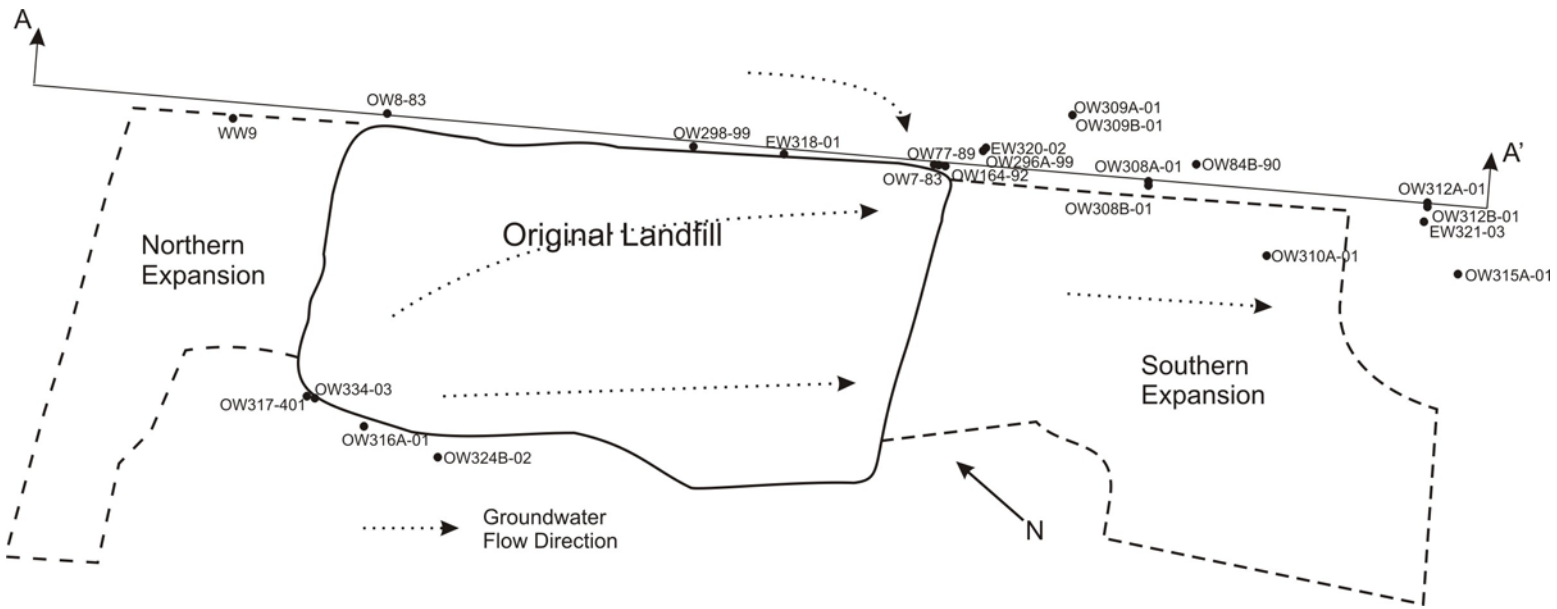


Figure 3.2 – Detailed plan view of cross section A-A’ at the Waterloo Landfill.

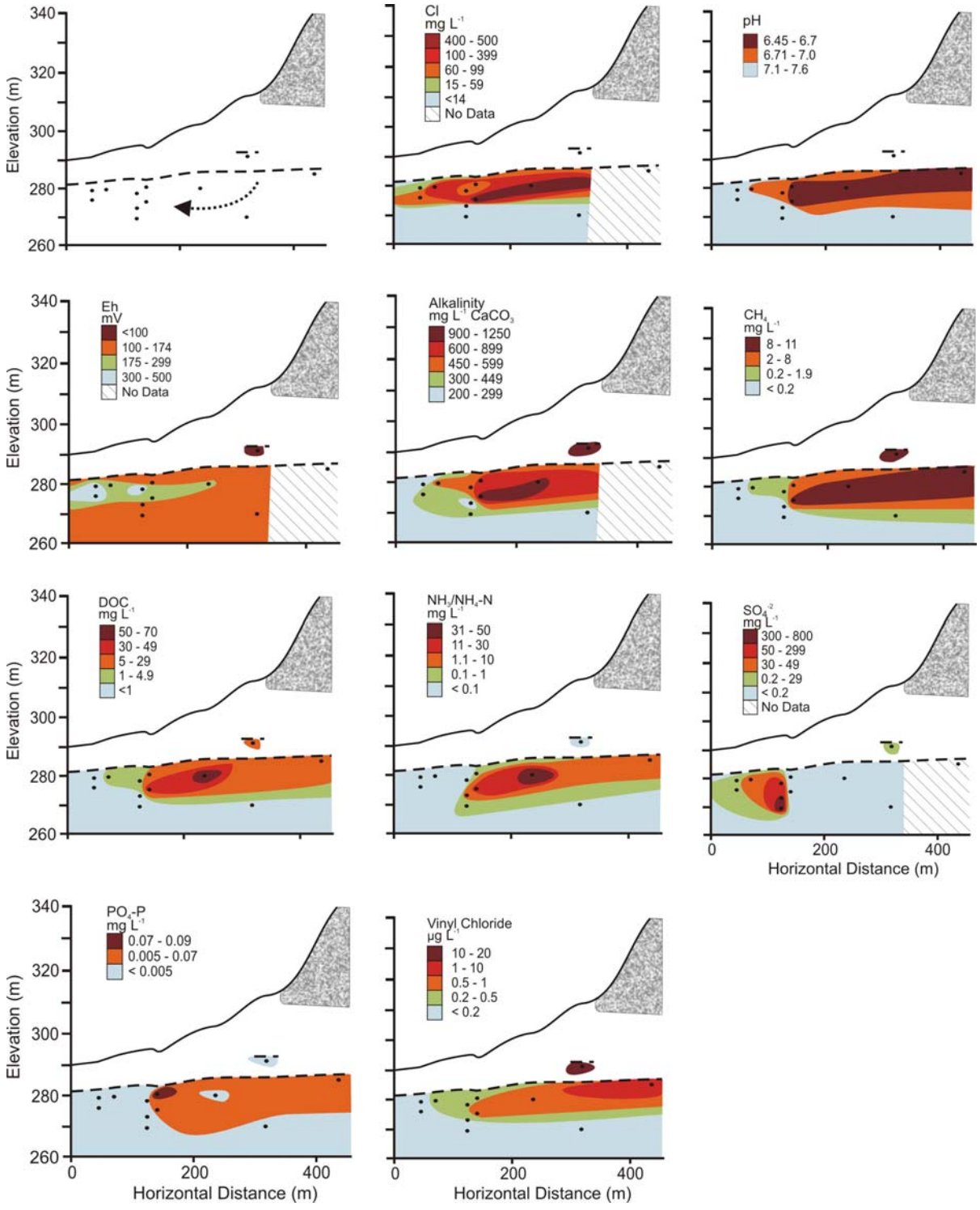


Figure 3.3 – Contours of geochemical parameters along C-C' at the Cambridge landfill. One well in a perched aquifer was also sampled. Results for vinyl chloride were obtained from the Region of Waterloo (CH2MHILL, 2008). There is a vertical exaggeration of 5.

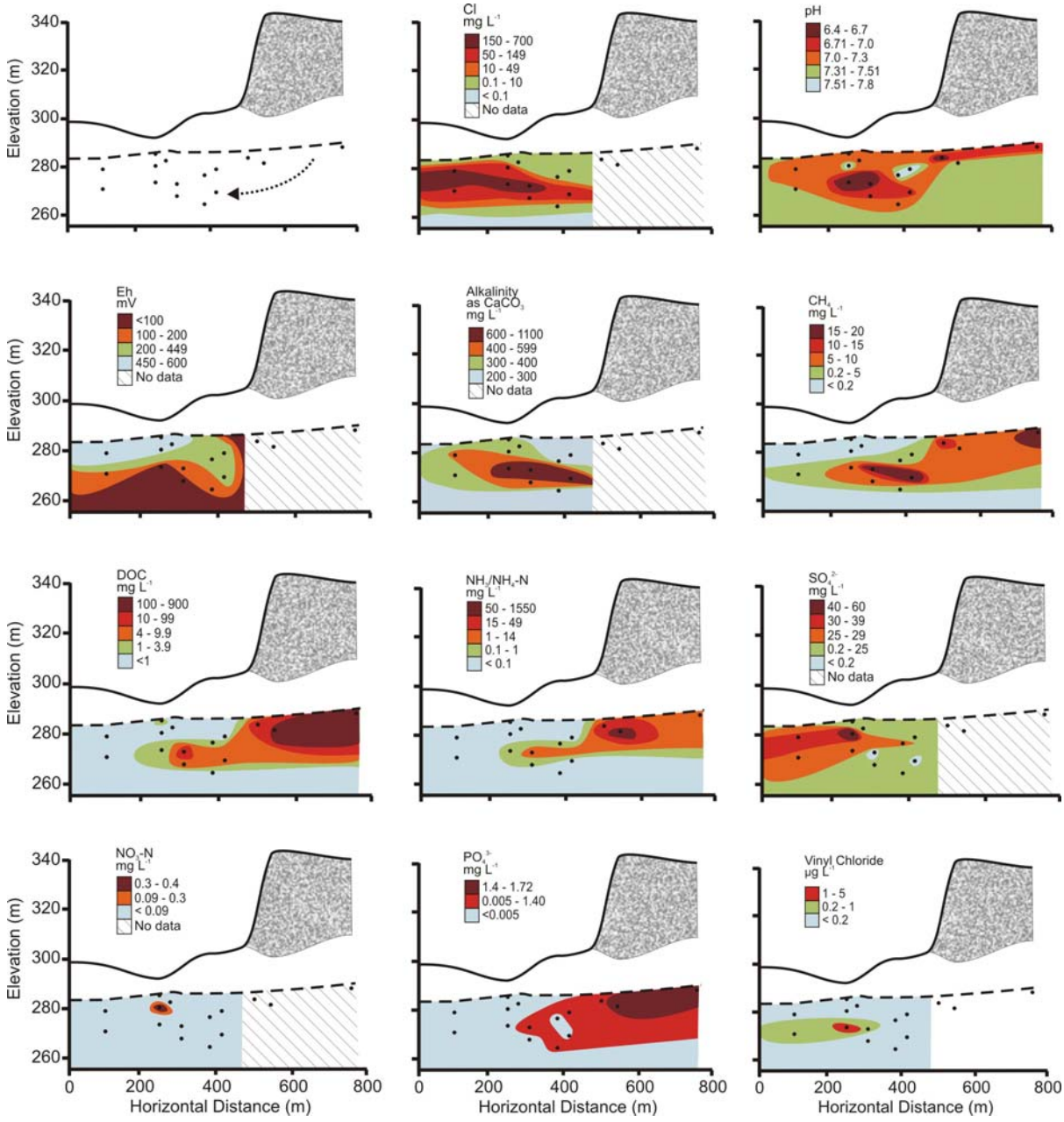


Figure 3.4 – Contours of geochemical parameters along cross section D-D' at the Cambridge. Vertical exaggeration of 7. Black dots represents sampling points. Results for vinyl chloride were obtained from the Region of Waterloo (CH2MHILL, 2008).

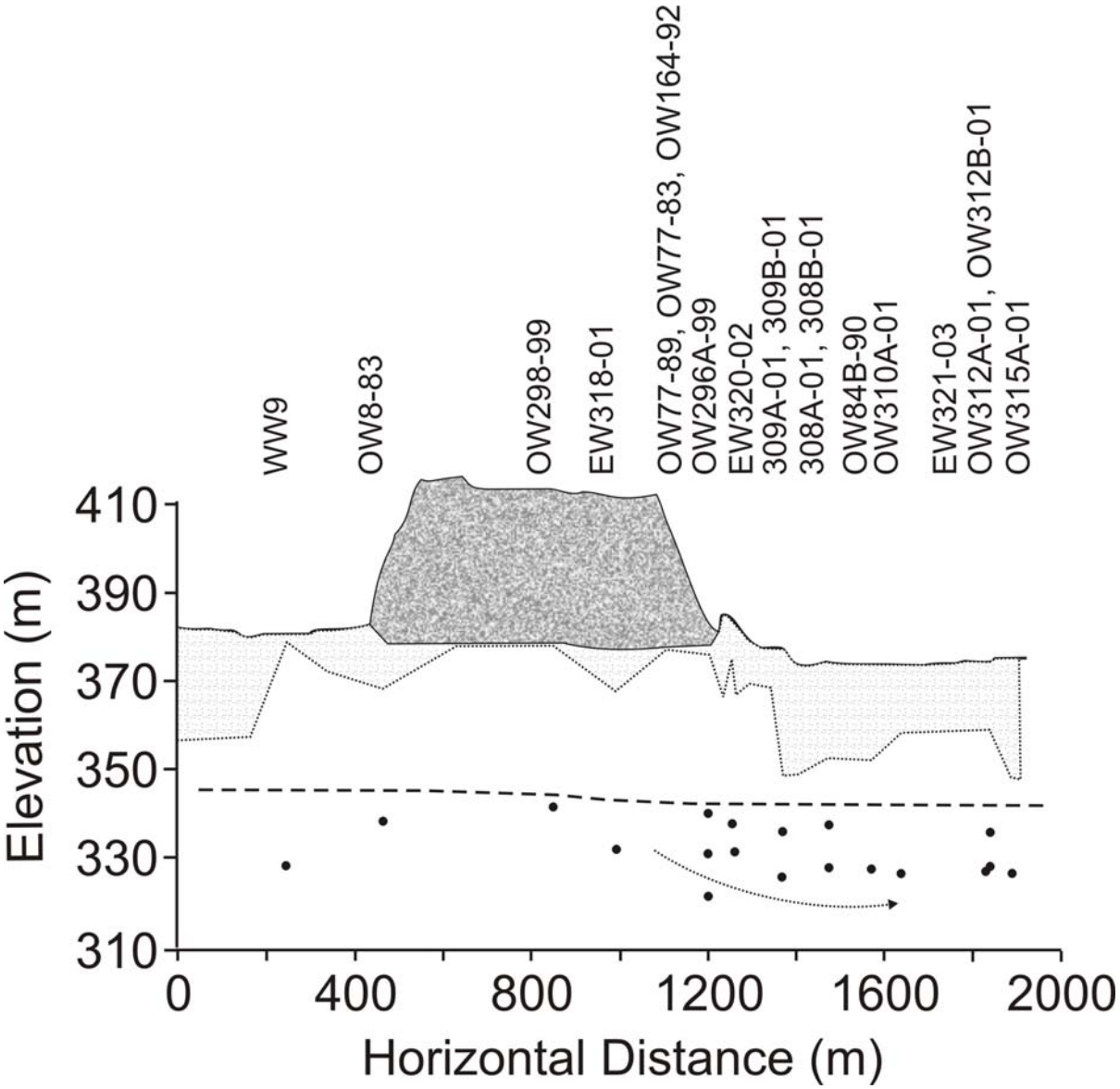


Figure 3. 5 – Detailed cross section for A-A' at the Waterloo Landfill illustrating the location of all sampling points.

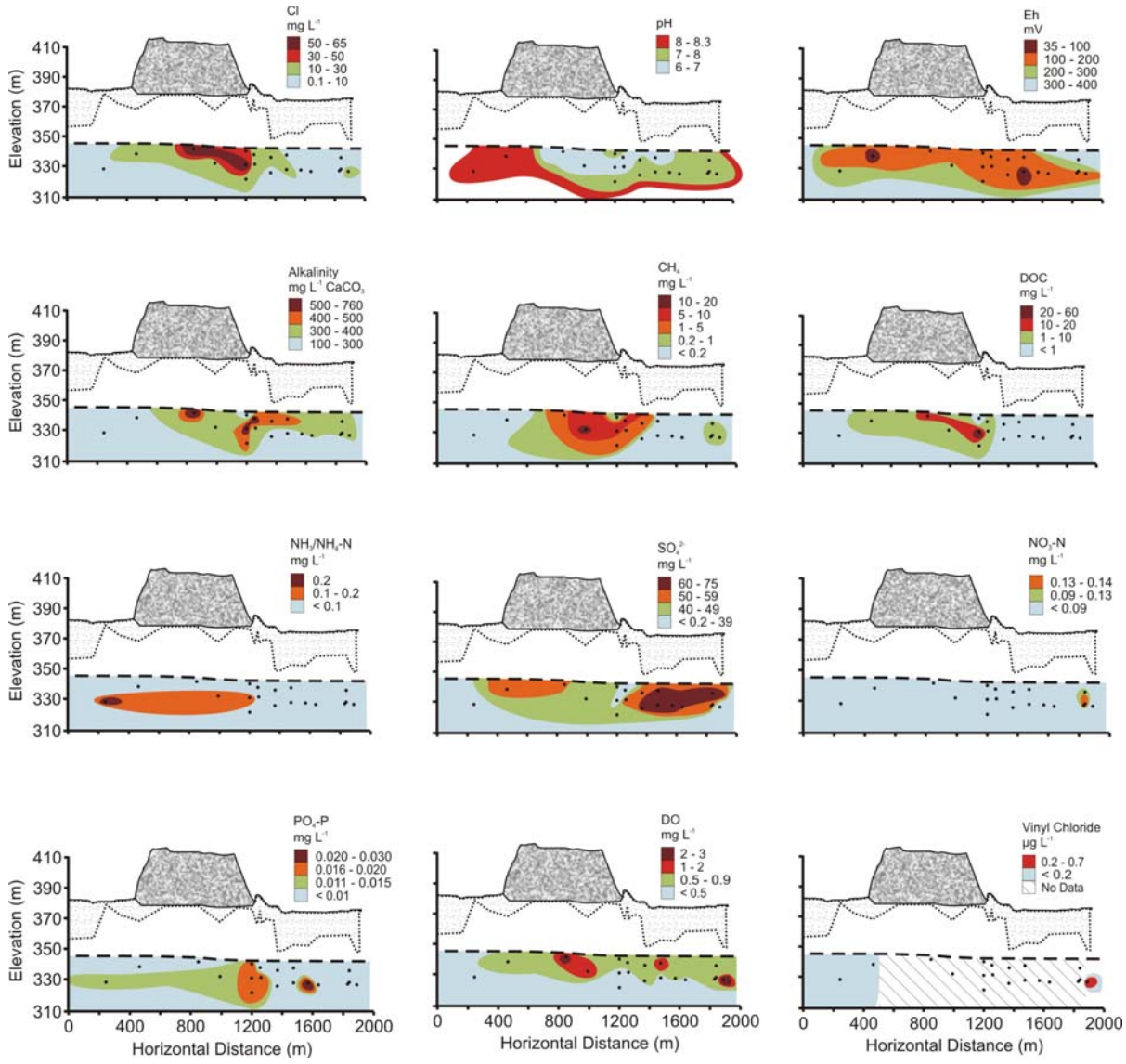


Figure 3.6 – Contours of geochemical parameters along cross section A-A' at the Waterloo Landfill. Results presented for vinyl chloride were obtained from the Region of Waterloo (Region of Waterloo, 2008).

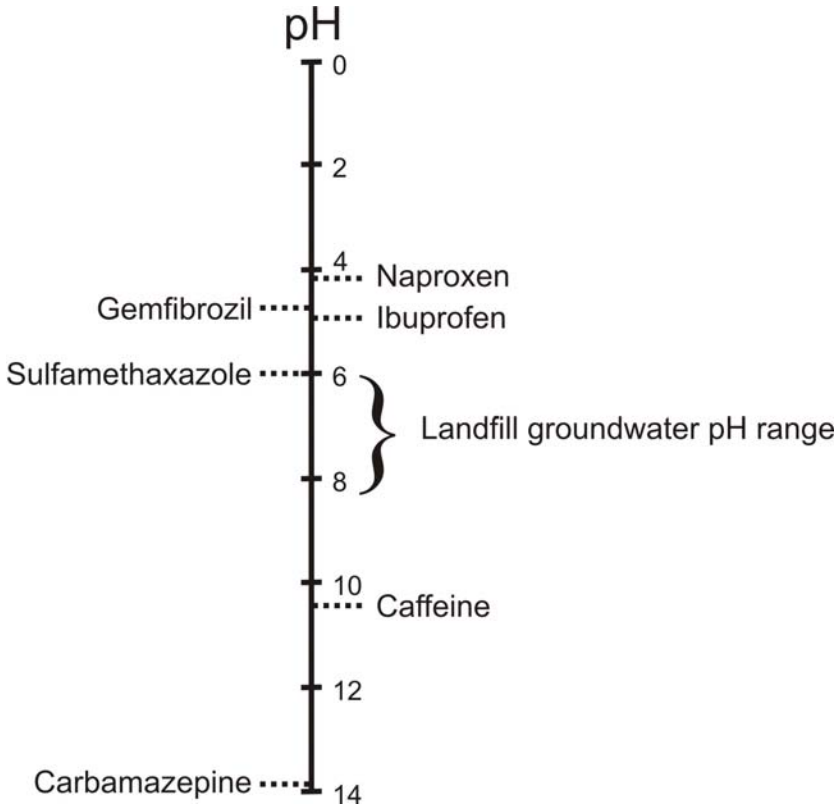


Figure 3.7 – pK_a of each pharmaceutical of interest plotted on the pH scale. The pH range of groundwater at the Cambridge and Waterloo Landfills (6.0 – 8.3) is noted.

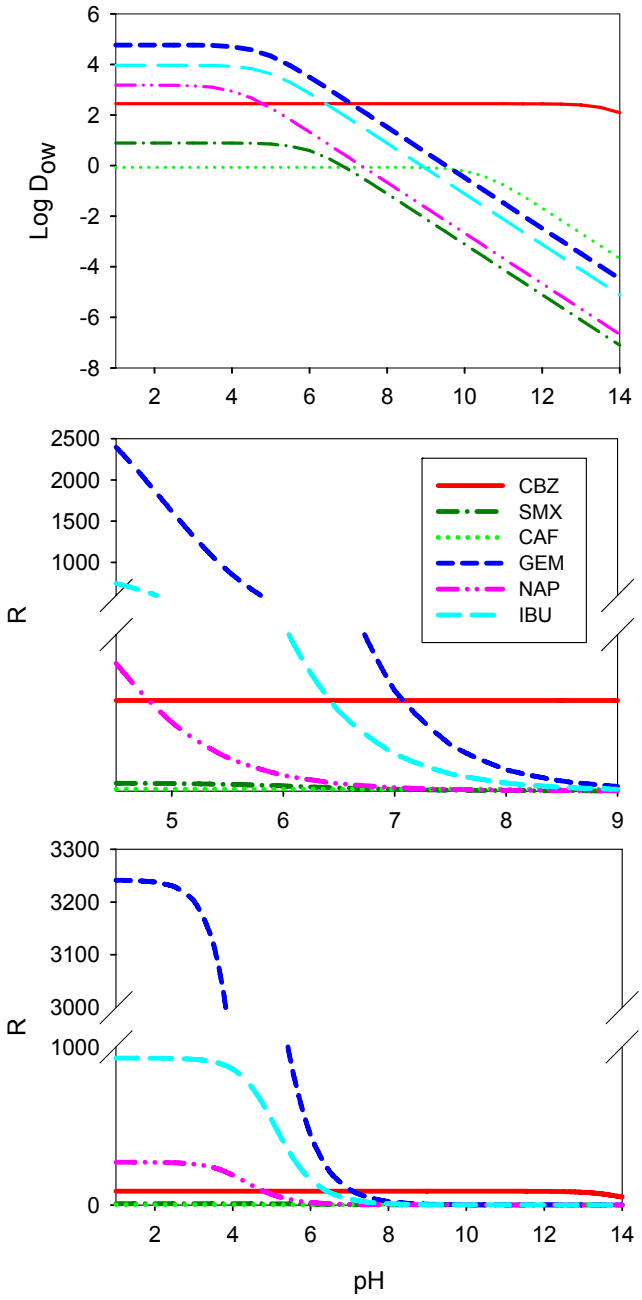


Figure 3.8 – The pH dependant partitioning coefficient (D_{ow}) was calculated for carbamazepine (CBZ), sulfamethoxazole (SMX), caffeine (CAF), ibuprofen (IBU), naproxen (NAP) and gemfibrozil (GEM) across the entire pH range. Retardation (R) values across the entire pH range, as well as typical pH values in a waste pile, were also calculated. A series of assumptions for waste were used in this calculation, including a bulk density of 0.65 g cm^{-3}, porosity of 0.4, organic carbon fraction of 25 %, and the assumption that the waste is fully saturated. Due to the assumptions in this calculation, the retardation coefficients were interpreted qualitatively only to obtain a relative indication of the effects of pH on R, and an indication of which drugs would be more retarded within the waste pile.

References

Chapter 1 References

CH2MHILL. 2008. Cambridge Landfill 2007 Annual Monitoring Review; Final Report. Prepared for Region of Waterloo.

Gros, M., Petrović, M., Barceló, D. 2007. Wastewater treatment plants as a pathway for aquatic contamination by pharmaceuticals in the Ebro River basin (Northeast Spain). Environ. Toxicol. Chem. 26 (8), 1553-1562.

Halling-Sørensen, B., Nors Nielsen, S., Launzky, P.F., Ingerslev, F., Holten Lützheft, H.C., Jørgensen, S.E. 1998. Occurrence, fate and effects of pharmaceutical substances in the environment – a review. Chemosphere 36 (2), 357-393.

Heberer, T. 2002. Occurrence, fate and removal of pharmaceutical residues in the aquatic environment: a review of recent research data. Toxicol. Lett. 131, 5-17.

Khetan, S.K., Collins, T.J. 2007. Human pharmaceuticals in the aquatic environment: A challenge to green chemistry. Chem. Rev. 107, 2319-2364.

Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B. Buxton, H.T. 2002. Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: A national reconnaissance. Environ. Sci. Technol. 36, 1202-1211.

Lissemore, L., Hao, C., Yang, P., Sibley, P.K., Mabury, S., Solomon, K.R. 2006. An exposure assessment for selected pharmaceuticals within a watershed in Southern Ontario. Chemosphere 64, 717-729.

Nikolaou, A., Meric, S., Fatta, D. 2007. Occurrence patterns of pharmaceuticals in water and wastewater environments. Anal. Bioanal. Chem. 387, 1225-1234.

Pedrouzo, M., Reverté, S., Borrull, F., Pocurull, E., Marcé, R. 2007. Pharmaceutical determination in surface and wastewaters using high-performance liquid chromatography-(electrospray)-mass spectrometery. J. Sep. Sci. 30, 397-303.

Rabiet, M., Togola, A., Brissaud, F., Siedel, J., Budzinski, H, Elbaz-Poulichet, F. 2006. Consequences of treated water recycling as regards pharmaceuticals and drugs in surface and ground waters of a medium-sized Mediterranean catchment. Environ. Sci. Technol. 40, 5282-5288.

Region of Waterloo. 2008. Waterloo Landfill Site, January 1 to December 31, 2007; Progress Report.

Strauch, G., Möder, M., Wennrich, R., Osenbrück, K., Gläser, H-R., Schladitz, T., Müller, C., Schirmer, K., Reinstorf, F., Schirmer, M. 2008. Indicators for assessing anthropogenic impact on urban surface and groundwater. J. Soils Sediments 8 (1), 23-33.

Vieno, N.M., Tuhkanen, T., Kronberg, L. 2006. Analysis of neutral and basic pharmaceuticals in sewage treatment plants and in recipient rivers using solid phase extraction and liquid chromatography-tandem mass spectrometry detection. J. Chromatogr. A 1134, 101-111.

Yu, J.T., Bouwer, E.J., Coelhan, M. 2006. Occurrence and biodegradability studies of selected pharmaceuticals and personal care products in sewage effluent. Agr. Water Manage. 86, 72-80.

Chapter 2 References

Appelo, C.A.J., Postma, D. 2006. Geochemistry, groundwater and pollution, 2nd edition. A. A. Balkema Publishers, New York, pp 326, 504

Aravena, R., Robsertson, W.D. 1998. Use of multiple isotope tracers to evaluate denitrification in groundwater: study of nitrate from a large flux septic system plume. Ground Water 36 (6), 975-982.

Bendz, D., Paxeus, N.A., Ginn, T.R., Loge, F.J. 2005. Occurrence and fate of pharmaceutically active compounds in the environment, a case study: Höje River in Sweden. J. Hazard. Mater. 122, 195-204.

Benotti, M.J., Brownawell, B.J. 2007. Distribution of pharmaceuticals in an urban estuary during both dry- and wet-weather conditions. Environ. Sci. Technol. 41, 5795-5802

Böhlke, J.K., Smith, R.L., Miller, D.M. 2006. Ammonium transport and reaction in contaminated groundwater: application of isotope tracers and isotope fractionation studies. Water Resour. Res. 42, 1-19.

Bound, J.P., Kitsou, K., Voulvoulis, N. 2006. Household disposal of pharmaceuticals and perception of risk to the environment. Environ. Toxicol. Pharmacol. 21, 301-307.

Bound, J.P, Voulvoulis, N. 2005. Household Disposal of pharmaceuticals as a pathway for aquatic contamination in the United Kingdom. Environ. Health Perspect. 113 (12), 1705-1711.

Broholm, M.M., Tuxen, N., Rügge, K., Bjerg, P.L. 2001. Sorption and degradation of the herbicide 2-methyl-4,6-dinitrophenol under aerobic conditions in a sandy aquifer in Vejen, Denmark. Environ. Sci. Technol. 35, 4789-4797.

Carrara, C., Ptacek, C.J., Robertson, W.D., Blowes, D.W., Moncur, M.C., Sverko, E., Backus, S. 2008. Fate of pharmaceutical and trace organic compounds in three septic system plumes, Ontario, Canada. Environ. Sci. Technol. 42, 2805-2811.

Collier, A.C. 2007. Pharmaceutical contaminants in potable water: potential concerns for pregnant women and children. EcoHealth 4, 164-171.

Conn, K.E., Barber, L.B., Brown, G.K., Siegrist, R.L. 2006. Occurrence and fate of organic contaminants during onsite wastewater treatment. Environ. Sci. Technol. 40, 7358-7366.
Heberer, T. 2002. Occurrence, fate and removal of pharmaceutical residues in the aquatic environment: a review of recent research data. Toxicol. Lett. 131, 5-17.

Drewes, J.E., Hebere, T., Reddersen, K. 2002. Fate of pharmaceuticals during indirect potable reuse. Water. Sci. Technol. 46 (3), 73-80.

Drewes, J.E., Heberer, T., Rauch, T., Reddersen, K. 2003. Fate of pharmaceuticals during groundwater recharge. Ground Water Monit. Rem. 23 (3), 64-72

Gerstl, Z. 1990. Estimation of organic chemical sorption to soils. J. Contam. Hydrol 6, 307-412

Godfrey, E., Woessner, W.W., Benotti, M.J. 2007. Pharmaceuticals in on-site sewage effluent and ground water, Western Montana. Ground Water 45 (3), 263-271.

Gros, M., Petrović, M., Barceló, D. 2007. Wastewater treatment plants as a pathway for aquatic contamination by pharmaceuticals in the Ebro River basin (Northeast Spain). Environ. Toxicol. Chem. 26 (8), 1553-1562.

Haderlein, S.B., Schwarzenbach, R.P. 1993. Adsorption of substituted nitrobenzenes and nitrophenols to mineral surfaces. Environ. Sci. Technol. 27, 316-326.

Halling-Sørsensen, B., Nielsen, S.N., Lanzky, P.F., Ingerslev, F., Holten Lützheft, H.C., Jørgensen, S.E. 1998. Occurrence, fate and effects of pharmaceutical substances in the environment – a review. Chemosphere 36 (2), 357-393

Hao, C., Lissemore, L., Nguyen, B., Kleywegt, S., Yang, P., Solomon, K. 2006. Determination of pharmaceuticals in environmental waters by liquid chromatography/electrospray ionization/tandem mass spectrometery. Anal. Bioanal. Chem. 384, 505-513.

Hebig, K. 2008. Transport behaviour of seven pharmaceuticals in groundwater. Diploma Thesis for Institut für Angewandte Geowissenschaften der Technischen Universität Berlin.

Hua, J., An, P., Winter, J., Gallart, C. 2003 . Elimination of COD, microorganisms and pharmaceuticals from sewage by trickling through sandy soil below leaky aquifers. Water Res. 37, 4395-4404.

Khetan, S.K., Collins, T.J. 2007. Human pharmaceuticals in the aquatic environment: A challenge to green chemistry. Chem. Rev. 107, 2319-2364.

Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B. Buxton, H.T. 2002. Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: A national reconnaissance. Environ. Sci. Technol. 36, 1202-1211.

Kreuzinger, N., Clara, M., Strenn, B., Vogel, B. 2004. Investigation on the behaviour of selected pharmaceuticals in the groundwater after infiltration of treated wastewater. Water Sci. Technol. 50 (2), 221-228.

Lissemore, L., Hao, C., Yang, P., Sibley, P.K., Mabury, S., Solomon, K.R. 2006. An exposure assessment for selected pharmaceuticals within a watershed in Southern Ontario. Chemosphere 64, 717-729.

Löffler, D., Römbke, J., Meuller, M.., Ternes, T.A. 2005. Environmental fate of pharmaceuticals in water/sediment systems. Environ. Sci. Technol. 39, 5209-5218.

Massmann, G., Dünnbier, U., Heberer, T., Taute, T. 2008. Behaviour of redox sensitivity of pharmaceutical residues during bank filtration – Investigations of residues of phenazone-type analgesics. Chemosphere 71, 1476-1485.

Ontario Water Resources Act. R.R.O. 1990. Regulation 903. Last amendment O. Reg. 372/07.

Osenbruck, K., Glaser, H.R., Knoller, K., Weise, S.M., Moder, M., Wennrich, R., Schirmer, M., Reinstorf, F., Busch, W. Strauch, G. 2007. Sources and transport of selected organic micropollutants in urban groundwater underlying the city of Halle (Saale), Germany. Water Res. 41, 3259-3270.

Pedrouzo, M., Reverté, S., Borrull, F., Pocurull, E., Marcé, R. 2007. Pharmaceutical determination in surface and wastewaters using high-performance liquid chromatography-(electrospray)-mass spectrometery. J. Sep. Sci. 30, 397-303.

Ptacek, C.J. 1998. Geochemistry of a septic-system plume in a coastal barrier bar, Point Pelee, Ontario, Canada. J. Contam. Hydrol. 33, 293-312.

Rabiet, M., Togola, A., Brissaud, F., Siedel, J., Budzinski, H, Elbaz-Poulichet, F. 2006. Consequences of treated water recycling as regards pharmaceuticals and drugs in surface and ground waters of a medium-sized Mediterranean catchment. Environ. Sci. Technol. 40, 5282-5288.

Repert, D.A., Barber, L.B., Hess, K.M., Keefe, S. H., Kent, D. B., Leblanc, D.R., Smith, R.L. 2006. Long-term natural attenuation of carbon and nitrogen within a groundwater plume after removal of the treated wastewater source. Environ. Sci. Technol 40, 1154-1162.

Robertson, W.D. 2008. Irreversible phosphorus sorption in septic system plumes? Ground Water 34 (2), 51-60.

Robertson, W.D., Blowes, D.W., Ptacek, C.J., Cherry, J.A. 2000. Long-term performance of insitu reactive barriers for nitrate remediation. Ground Water 38 (5), 689-695.

Robertson, W.D., Harman, J. 1999. Phosphate plume persistence at two decommissioned septic system sites. Ground Water 37 (2), 228-236.

RxList Inc., November 2008. The internet drug index. Available: www.rxlist.com

Scheytt, T., Mersmann, P., Lindstadt, R., Heberer, T. 2005. Determination of sorption coefficients of pharmaceutically active substances carbamazepine, diclofenac and ibuprofen, in sandy sediments. Chemosphere 60, 245-253.

Scheytt, T.J., Mersmann, P., Heberer, T. 2006. Mobility of pharmaceuticals carbamazepine, diclofenac, ibuprofen and propyphenazone in miscible-displacement experiments. J. Contam. Hydrol. 83, 53-69.

Scheytt, T.J., Mersmann, P., Rejman-Rasinski, E., These, A. 2007. Tracing pharmaceuticals in the unsaturated zone. J. Soils Sediments 7 (2), 75-84.

Siebert, S. 2007. Degradation and sorption of the pharmaceutical carbamazepine. Diploma Thesis for Institut für Angewandte Geowissenschaften der Technischen Universität Berlin.

Siemens, J., Huschek, G., Siebe, C., Kaupenjohann, M. 2008. Concentrations and mobility of human pharmaceuticals in the world's largest wastewater irrigation system, Mexico City-Mezquital Valley. Water Res. 42, 2124-2134.

Slack, R.J., Bonin, M., Gronow, J.R., Van Santen, A., Voulvoulis, N. 2007. Household hazardous waste data for the UK by direct sampling. Environ. Sci. Technol. 41, 2566-2571.

Stafiej, A., Pyrzynska, K., Regan, F. 2007. Determination of anti- inflammatory drugs and estrogens in water by HPLC with UV detection. J.Sep.Sci. 30, 985-991.

Stoob, K., Singer, H.P., Mueller, S.R., Schwarzenbach, R.P., Stamm, C.H. 2007. Dissipation and transport of veterinary sulfonamide antibiotics after manure application in a small catchment. Environ. Sci. Technol. 41, 7349-7355.

Stuer-Lauridsen, F., Birkved, M., Hansen, L.P., Holten Lützhoft, H.-C., Halling-Sørensen, B. 2000. Environmental risk assessment of human pharmaceuticals in Denmark after normal therapeutic use. Chemosphere 40, 783-793.

Suntisukaseam, U., Weschayanwi, P., Sabatini, D.A. 2007. Sorption of amphiphile pharmaceutical compounds onto polar and non-polar absorbents. Environ. Eng. Sci. 24 (10), 1457-1466.

Swartz, C.H., Reddy, S., Benotti, M.J., Yin, H., Barber, L.B., Brownawell, B.J., Rudel, R.A. 2006. Steroid estrogens, nonylphenol ethoxylate metabolites, and other wastewater contaminants in groundwater affected by a residential septic system on Cape Cod, MA. Environ. Sci. Technol. 40, 4895-4902.

Tappe, W., Zarfl, C., Kummer, S., Burauel, P., Vereecken, H., Groeneweg, J. 2008. Growth-inhibitory effects of sulfonamides at different pH: Dissimilar susceptibility patterns of a soil bacterium and a test bacterium used for antibiotic assays. Chemosphere 72, 836-843.

Ternes, T.A. 1998. Occurrence of drugs in German sewage treatment plants and rivers. Water Res. 32, 3245-3260.

Trenholm, R.A., Vanderford, B.J., Holady, J.C., Rexing, D.J., Snyder, S.A. 2006. Broad range analysis of endocrine disruptors and pharmaceuticals using gas chromatography and liquid chromatography tandem mass spectrometry. Chemosphere 65, 1990-1998.

Vanderford, B.J., Pearson, R.A., Rexing, D.J., Snyder, S.A. 2003. Analysis of endocrine disruptors, pharmaceuticals, and personal care products in water using liquid chromatography/ tandem mass spectrometry. Anal. Chem 75, 6265-6574.

Vieno, N.M., Tuhkanen, T., Kronberg, L. 2006. Analysis of neutral and basic pharmaceuticals in sewage treatment plants and in recipient rivers using solid phase extraction and liquid chromatography-tandem mass spectrometry detection. J. Chromatogr. A 1134, 101-111.

Wehrhan, A., Kasteel, R., Simunek, J., Groeneweg, J., Vereecken, H. 2007. Transport of sulfadiazine in soil columns – experiments and modeling approaches. J. Contam. Hydrol. 89, 107-135.

Yu, J.T., Bouwer, E.J., Coelhan, M. 2006. Occurrence and biodegradability of studies of selected pharmaceuticals and personal care products in sewage effluent. Agr. Water Manage. 86, 72-80.

Zanini, L., Robertson, W.D., Ptacek, C.J., Schiff, S.L., Mayer, T. 1998. Phosphorous characterization in sediments impacted by septic effluents at four sites in central Canada. J. Contam. Hydrol. 33, 405-429.

Chapter 3 References

Ahel, T., Mijatović, I., Matošić, M., Ahel, M. 2004. Nanofiltration of a landfill leachate containing pharmaceutical intermediates from vitamin C production. Food Technol. Biotechnol 42 (2), 99-104.

Barnes, K.K., Christenson, S.C., Kolpin, D.W., Focazio, M.J., Furlong, E.T., Zaugg, S.D., Meyer, M.T., Barber, L.B. 2004. Pharmaceuticals and other organic waste water contaminants within a leachate plume downgradient of a municipal landfill. Ground Water Monit. Remed. 24 (2), 119-126.

Biersteker, J. 2008. Region of Waterloo. Personal communication.

Bjerg, P.L., Albrechtsen, H.-J., Kjeldsen, P., Christensen, T.H, Cozzarelli, I.M.. 2005. The groundwater geochemistry of waste disposal facilities. In: Treatise on Geochemistry (B.S. Lollar, Ed.) Vol 9: Environmental Geochemistry, pp 579-612.

Blicher-Mathiesen, G., McCarty, G.W., Nielsen, L.P. 1998. Denitrification and degassing in groundwater estimated from dissolved dinitrogen and argon. J. Hydrol. 208, 16-24.

Bound, J.P, Voulvoulis, N. 2005. Household disposal of pharmaceuticals as a pathway for aquatic contamination in the United Kingdom. Environ. Health Perspect. 113 (12), 1705-1711.

Bound, J.P., Kitsou, K., Voulvoulis, N. 2006. Household disposal of pharmaceuticals and perception of risk to the environment. Environ. Toxicol. Pharmacol. 21, 301-307.

Carrara, C., Ptacek, C.J., Robertson, W.D., Blowes, D.W., Moncur, M.C., Sverko, E., Backus, S. 2008. Fate of pharmaceutical and trace organic compounds in three septic system plumes, Ontario, Canada. Environ. Sci. Technol. 42, 2805-2811.

Christensen, T.H., Kjeldsen, P., Bjerg, P.L., Jensen, D.L., Christensen, J.B., Baun, A., Albrechtsen, H.-J., Heron, G. 2001. Biogeochemistry of landfill leachate plumes. Appl. Geochem. 16, 659-718.

CH2MHILL. 2008. Cambridge Landfill 2007 Annual Monitoring Review; Final Report. Prepared for Region of Waterloo.

Díaz-Cruz, M.S., García-Galán, M.J., Barceló, S. 2008. Highly sensitive simultaneous determination of sulfonamide antibiotics and one metabolite in environmental waters by liquid chromatography-quadrupole linear ion trap-mass spectrometery. J. Chromatog. A 1193, 50-59.

Doerr-MacEwen, N.A., Haight, M.E. 2006. Expert stakeholders' views on the management of human pharmaceuticals in the environment. Environ. Management 38, 853-866

Drewes, J.E., Heberer, T., Rauch, T., Reddersen, K. 2003. Fate of pharmaceuticals during ground water recharge. Ground Water Monit. Remed. 23 (3), 64-72.

Eckel, W.P., Ross, B., Isensee, R.K. 1993. Pentobarbital found in groundwater. Ground Water 31 (5), 801-804.

Environment Canada. 1996. The State of Canada's Environment, Urban Environment, Solid Waste. Accessible at http://www.ec.gc.ca/soer-ree/English/SOER/1996report/Doc/1-7-5-5-5-2-1.cfm.

Feitosa-Felizzola, J., Temime, B., Chiron, S. 2007. Evaluation on-line solid-phase extraction coupled to liquid chromatography-ion trap mass spectrometry for reliable quantification and confirmation of several classes of antibiotics in urban wastewaters. J.Chromatog.A 1164, 95-104.

Fenz, R., Blaschke, A.P., Clara, M., Kroiss, H., Mascher, D., Zessner, M. 2005. Monitoring of carbamazepine concentrations in wastewater and groundwater to quantify sewer leakage. Water Sci. Technol. 52 (5), 205-213

Godfrey, E., Woessner, W.W., Benotti, M.J. 2007. Pharmaceuticals in on-site sewage effluent and ground water, Western Montana. Ground Water 45 (3), 263-271.

Halford, B. 2008. Don't Flush; what to do with your unused medications. Chem. Eng. News 86 (8), 16.

Halling-Sørsensen, B., Nielsen, S.N., Lanzky, P.F., Ingerslev, F., Holten Lützheft, H.C., Jørgensen, S.E. 1998. Occurrence, fate and effects of pharmaceutical substances in the environment – a review. Chemosphere 36 (2), 357-393

Hao, C., Lissemore, L., Nguyen, B., Kleywegt, S., Yang, P., Solomon, K. 2006. Determination of pharmaceuticals in environmental waters by liquid chromatography/electrospray ionization/tandem mass spectrometery. Anal. Bioanal. Chem. 384, 505-513.

Heberer, T. 2002. Occurrence, fate and removal of pharmaceutical residues in the aquatic environment: a review of recent research data. Toxicol. Lett. 131, 5-17.

Hebig, K. 2008. Transport behaviour of seven pharmaceuticals in groundwater. Diploma Thesis for Institut für Angewandte Geowissenschaften der Technischen Universität Berlin.

Holm, J.V., Rügge, K., Bjerg, P.L., Christensen, T.H. 1995. Occurrence and distribution of pharmaceutical organic compounds in the groundwater downgradient of a landfill (Grindsted, Denmark). Environ. Sci. Technol. 29 (5), 1415-1420.

Khetan, S.K., Collins, T.J. 2007. Human pharmaceuticals in the aquatic environment: A challenge to green chemistry. Chem. Rev. 107, 2319-2364.

Kjeldsen, P., Barlaz, M.A., Rooker, A.P., Baun, A., Ledin, A., Christensen, T.H. 2002. Present and long-term composition of MSW landfill leachate: A review. Crit. Rev. Environ. Sci.Technol. 32 (4), 297-336.

Kreuzinger, N., Clara, M., Strenn, B., Vogel, B. 2004. Investigation on the behaviour of selected pharmaceuticals in the groundwater after infiltration of treated wastewater. Water Sci. Technol. 50 (2), 221-228.

Lee, J.-Y., Cheon, J.-Y., Kwon, H.-P., Yoon, H.-S., Lee, S.-S., Kim, J.-H., Park, J.-K., Kim, C.-G. 2006. Attenuation of landfill leachate at two uncontrolled landfills. Environ. Geol. 51, 581-593.

Lishman, L., Smyth, S.A., Sarafin, K., Kleywegt, S., Toito, J., Peart, T., Lee, B, Servos, M., Beland, M., Seto, P. 2006. Occurrence and reductions of pharmaceuticals and personal care products and estrogens by municipal wastewater treatment plants in Ontario, Canada. Sci. Tot. Environ. 367, 544-558.

Lissemore, L., Hao, C., Yang, P., Sibley, P.K., Mabury, S., Solomon, K.R. 2006. An exposure assessment for selected pharmaceuticals within a watershed in Southern Ontario. Chemosphere 64, 717-729.

Metcalfe, C.D., Koenig, B.G., Bennie, D.T., Servos, M., Ternes, T.A., Hirsch, R. 2003. Occurrence of neutral and acidic drugs in the effluents of Canadian sewage treatment plants. Environ. Toxicol. Chem. 22 (12), 2872-2880.

Nikolaou, A., Meric, S., Fatta, D. 2007. Occurrence patterns of pharmaceuticals in water and wastewater environments. Anal. Bioanal. Chem. 387, 1225-1234.

Pedrouzo, M., Reverté, S., Borrull, F., Pocurull, E., Marcé, R. 2007. Pharmaceutical determination in surface and wastewaters using high-performance liquid chromatography-(electrospray)-mass spectrometery. J. Sep. Sci. 30, 397-303.

Region of Waterloo. 2008. Waterloo Landfill Site, January 1 to December 31, 2007; Progress Report.

Scheytt, T.J., Mersmann, P., Heberer, T. 2006. Mobility of pharmaceuticals carbamazepine, diclofenac, ibuprofen and propyphenazone in miscible-displacement experiments. J. Contam. Hydrol. 83, 53-69.

Scheytt, T.J., Mersmann, P., Rejman-Rasinski, E., These, A. 2007. Tracing pharmaceuticals in the unsaturated zone. J. Soils Sediments 7 (2), 75-84.

Schwarzbauer, J., Heim, S., Brinker, S., Littke, R. 2002. Occurrence and alteration of organic contaminants in seepage and leakage water from a waste deposit landfill. Water Res. 36, 2275-2287.

Seehusen, D.A., Edwards, J. 2006. Patient practices and beliefs concerning disposal of medications. J. Am. Board. Fam. Med. 19, (6), 542-547.

Seiler, R.L., Zaugg, S.D., Thomas, J.M., Howcroft, D.L. 1999. Caffeine and pharmaceuticals as indicators of waste water contamination in wells. Ground Water 37 (3), 405-410.

Siemens, J., Huschek, G., Siebe, C., Kaupenjohann, M. 2008. Concentrations and mobility of human pharmaceuticals in the world's largest wastewater irrigation system, Mexico City-Mezquital Valley. Water Res. 42, 2124-2134.

Slack R.J., Gronow, J.R., Hall, D.H., Voulvoulis, N. 2007a. Household hazardous waste disposal to landfill: using LandSim to model leachate migration. Environ. Poll. 146, 501-509.

Slack, R.J., Bonin, M., Gronow, J.R., Van Santen, A., Voulvoulis, N. 2007b. Household hazardous waste data for the UK by direct sampling. Environ. Sci. Technol. 41, 2566-2571.

Snyder, S.A., Leising, J., Westerhoff, P., Yoon, Y., Mash, H., Vanderford, B. 2004. Biological and physical attenuation of endocrine disruptors and pharmaceuticals: Implications for water reuse. Ground Water Monit. Remed. 24 (2), 108-118.

Stuer-Lauridsen, F., Birkved, M., Hansen, L.P., Holten Lützhoft, H.-C., Halling-Sørensen, B. 2000. Environmental risk assessment of human pharmaceuticals in Denmark after normal therapeutic use. Chemosphere 40, 783-793.

Vanderford, B.J., Snyder, S.A. 2006. Analysis of pharmaceuticals in water by isotope dilution liquid chromatography/tandem mass spectrometry. Environ. Sci. Technol. 40, 7312-7320.

APPENDIX A: SEPTIC SYSTEM DESIGN AND FUNCTION

The processes considered in the design and function of typical septic beds are summarized as follows (Willhem et al., 1994): Conventional septic systems are designed to have three different zones, an anaerobic zone, an aerobic zone, and (sometimes) a second anaerobic zone. The first anaerobic zone consists of the septic tank and a layer of accumulated organic matter below the distribution pipes, known as the biological mat. Retention times in the septic tank are typically designed to be at least 24 hours. Within the tank, physical treatment occurs through the settling of dense particles to create sludge, and floating particles are retained by hanging barriers, forming scum. The tank remains mainly anaerobic despite the fact that it is vented due to the low diffusion coefficient of oxygen, which is further inhibited by the floating scum. Therefore, any oxidation of reduced species, specifically organic matter, in the tank occurs anaerobically. This biochemical treatment occurs through a variety of steps, the first of which involves microbially mediated hydrolyzation of large organic molecules into simpler molecules such as amino acids, sugars, and fatty acids. The sugars and amino acids are then fermented, meaning organic carbon is oxidized and reduced to produce intermediate organic acids, acetate, and H_2. The fatty acids and intermediate organic acids then undergo anaerobic oxidation, accepting protons to form H_2. Finally, methanogenic bacteria in the tank use the acetate or CO_2 and H_2 to produce CH_4 and CO_2. The septic tank wastewater is discharged to the tile lines by gravity or pumps, where it infiltrates into the unsaturated zone. Directly below the tile lines, a biological mat typically forms. This mat strains out the suspended particles and organic matter, resulting in a build up of the mat over time, potentially slowing the rate of infiltration of wastewater into the aquifer. Oxygen ingress into the mat is often limited during periods of high loadings. The

processes that occur during this anaerobic stage tend to maintain a near-neutral pH, and the alkalinity of the waste water also remains fairly stable.

Once the wastewater passes through the biological mat, it contacts increased concentrations of oxygen, which allows for aerobic degradation reactions to occur. Because organic carbon (CH_2O) and NH_4 are thermodynamically unstable where O_2 is available, they tend to readily oxidize. In general, the limiting factor is the available O_2, therefore it is important that the aerobic zone is sufficiently thick to promote oxidation reactions. When NH_4 is oxidized to NO_3^-, the pH and alkalinity are affected since $2H^+$ ions are released into solution for every one mol of NH_4 consumed. The oxidation of CH_2O produces CO_2, which decreases pH if it remains in solution, but only alters the alkalinity if it leads to $CaCO_3$ dissolution. Removal of organic carbon and nitrogen may also occur through direct reaction with the aquifer materials, however this removal is believed to occur to a lesser extent.

After the aerobic degradation of NH_4 and CH_2O occurs, some systems may possess a second anaerobic zone known as the denitrification zone. In this zone, the nitrate produced during oxidation of NH_4 would be reduced to N_2 gas, which is unavailable to most organisms. This denitrification occurs by bacteria that require anoxic conditions to reduce NO_3, therefore it would typically occur in saturated or near saturated sediments due to limited O_2 diffusion. This process rarely occurs, however, because organic carbon is also needed to drive the reaction, but if the system is designed correctly, all the organic carbon should have been consumed during the aerobic stage when the NO_3 itself was produced. Therefore, typically

aquifers with a high fraction of organic carbon are the only environments where a denitrifying zone would develop.

Therefore, the best treatment of the major wastewater constituents occurs if all three zones are achieved, since then not only is organic carbon being removed, but so is nitrate. Potential problems that arise in the design and functioning capabilities of a septic bed include a fluctuating water table limiting the extent of the aerobic zone, a gradual loss of buffering capacity, allowing low pH conditions to develop, increasing metal mobility or inhibiting microbial activity.

Reference:

Wilhelm, S.R., Schiff, S.L., Cherry, J.A. 1994. Biogeochemical evolution of domestic waste water in septic systems: 1. Conceptual model. Ground Water 32 (6), 905-916.

APPENDIX B: ANALYSIS OF FREEZING AND STORAGE OF SOLID PHASE EXTRACTIONS ON CARBAMAZEPINE CONCENTRATIONS

In evaluating for the presence of various pharmaceuticals in the groundwater at this site, a variety of methodology tests were performed using the drug carbamazepine as a representative analyte. One test investigated the effect of processing the sample immediately following collection, versus long-term storage through freezing, thawing, re-filtering and then analyzing. An additional test that was conducted considered the impact of the age of the MeOH preserved solid phase extraction (SPE) eluate on the results obtained compared to results processed soon after SPE for the frozen samples.

Effect of Freezing

When evaluating the effect of freezing, thawing, and subsequently re-filtering with 0.45 μm nylon filters prior to sample preparation by SPE, results for samples frozen for approximately 2 months (frozen samples) were compared to results for carbamazepine from a sample processed immediately after collection from the field and storage at 4°C until sample preparation by SPE (fresh samples). No substantial visual difference between the carbamazepine plumes of the fresh and frozen sample sets was observed (Figure B.1), indicating that for the purpose of this analysis, either fresh or frozen samples are sufficient for purposes of data interpretation for carbamazepine. In each preparation scenario calibrations were strong, having accuracies close to 100% (+/- 5%), with strong correlation coefficients (>0.999) (Table 2.2). The percent difference between carbamazepine concentrations in fresh and frozen samples is plotted in Figure B.2. The median of the percent difference between results was satisfactory at 14 %, while the average was significantly higher at 51 %. The large difference in these statistics is the result of several samples which had substantially different carbamazepine concentrations, some of which

were run in duplicate or triplicate, thus having a greater influence on the average. For the several samples run in triplicate that had a vast difference in concentrations, the frozen samples tended to have a much lower concentration than the fresh sample. It is unclear why the results for several samples showed large differences, while the results for the majority of samples were relatively unaffected by the freezing and filtering process.

Storage of SPE Eluate

When investigating the drug carbamazepine, duplicate analyses of the frozen samples were conducted, allowing for comparison of results for samples processed soon after SPE, to up to 6 months after. SPE eluate was stored at 4°C for 6 months prior to being re-analyzed. The contoured diagrams showing the influence of holding time on the analyses indicate negligible differences in the visual analyses at the plume scale (Figure B.3).

A comparison of concentrations for carbamazepine obtained for the sample processed immediately after SPE relative to concentrations for the same samples re-analyzed 6 months later illustrates that the majority of the concentrations are similar (Table B.1). The per cent difference between the two analyses illustrates this trend, with a mean per cent difference of 16 % and a median percent difference of 14 %.

In summary, a preliminary overview of carbamazepine analysis suggests that freezing of samples and storage of SPE eluate does not influence the visual interpretation of the plume concentration contours. Further studies should be conducted for the other pharmaceuticals of

interest in this study (caffeine, sulfamethoxazole, naproxen, gemfibrozil, and ibuprofen) to determine the impact of freezing and storage of eluate on sample concentrations.

Long Point ID	CBZ Concentration (0 months)	CBZ Concentration (6 months)	% Difference
120 – 2.8	21	19	8
120 – 2.8	16	19	-19
120 – 3.4	520	460	12
120 – 3.9	1259	1065	17
120 - 4.6	876	747	16
120 - 5.3	506	476	6
121 - 2.6	318	291	9
121 - 3.2	935	771	19
121 - 3.8	1480	1280	14
121 - 4.4	941	830	13
121 - 5.0	994	835	17
122 - 2.8	445	460	-3
122 - 3.4	1200	930	25
122 - 4.6	1510	960	45
123 - 2.6	501	435	14
123 - 3.2	1080	824	27
123 - 3.8	2190	1510	37
123 - 4.5	13	16	-21
124 - 1.6	27	22	19
124 - 2.1	184	173	6
124 - 2.6	155	134	14
124 - 3.1	119	103	14
124 - 3.6	184	155	17
136 - 1.9	41	40	4
136 - 2.3	531	431	21
136 - 2.7	502	465	8
138 - 1.9	888	788	12
138 - 2.3	2060	2050	0
138 - 2.7	468	408	14
138 - 3.1	606	564	7
Tank	59	77	-26
		Absolute Average	16
		Absolute Median	14
		Absolute Standard Deviation	9

Table B.1 – Long Point groundwater concentrations for carbamazepine (CBZ) between samples analyzed immediately after solid phase extraction (SPE) (0 months) and the same sample rerun after storage of SPE eluate at 4°C for a period of 6 months (6 months). The percent difference between these two analytical runs indicates results are similar, with an average percent difference of 16 %, and a median per cent difference of 14 %. A positive percent difference indicates that eluate processed immediately after SPE had a higher concentration than eluate that was stored.

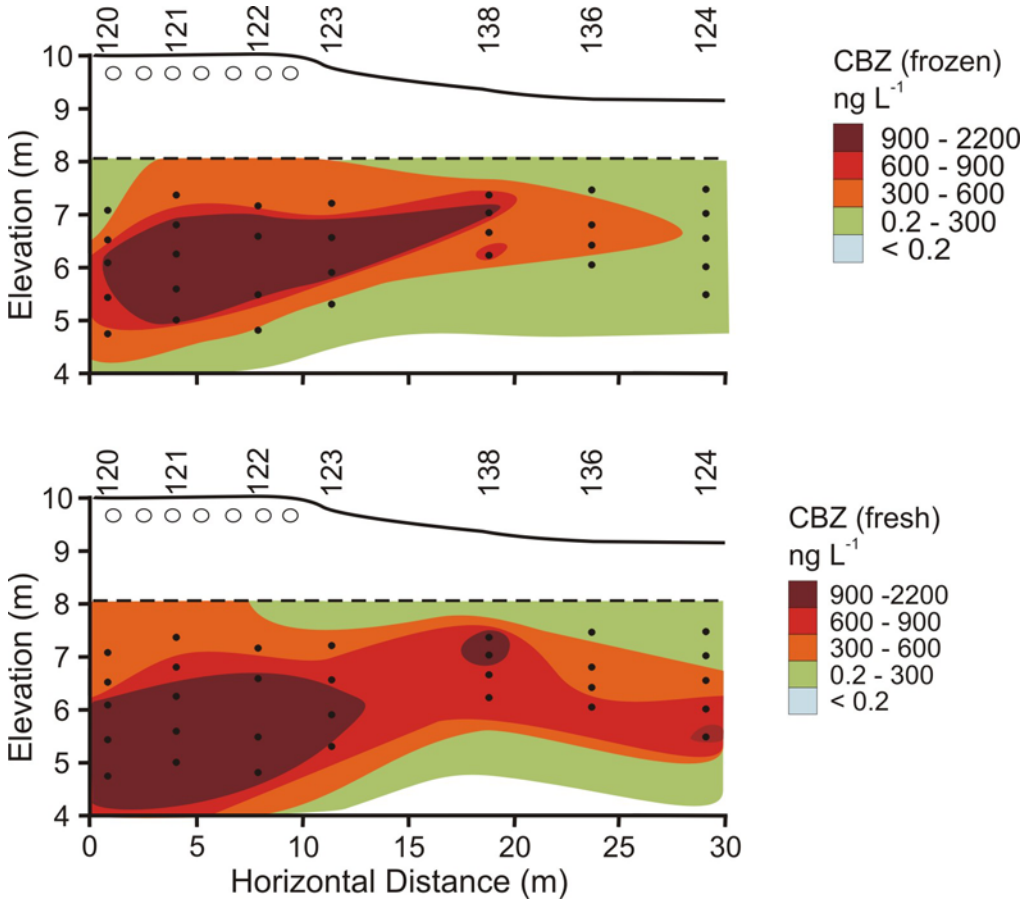


Figure B.1 – Carbamazepine (CBZ) plume delineations are provided for two separate samples from Long Point groundwater. The top plot is for a sample collected in the field, frozen, thawed, filtered, and then processed (frozen). The lower plot is for a sample processed directly after collection, without being frozen or re-filtered (fresh). While there is some variation in the plume, overall, the trends are the same, allowing for similar visual interpretation between the two sets of samples.

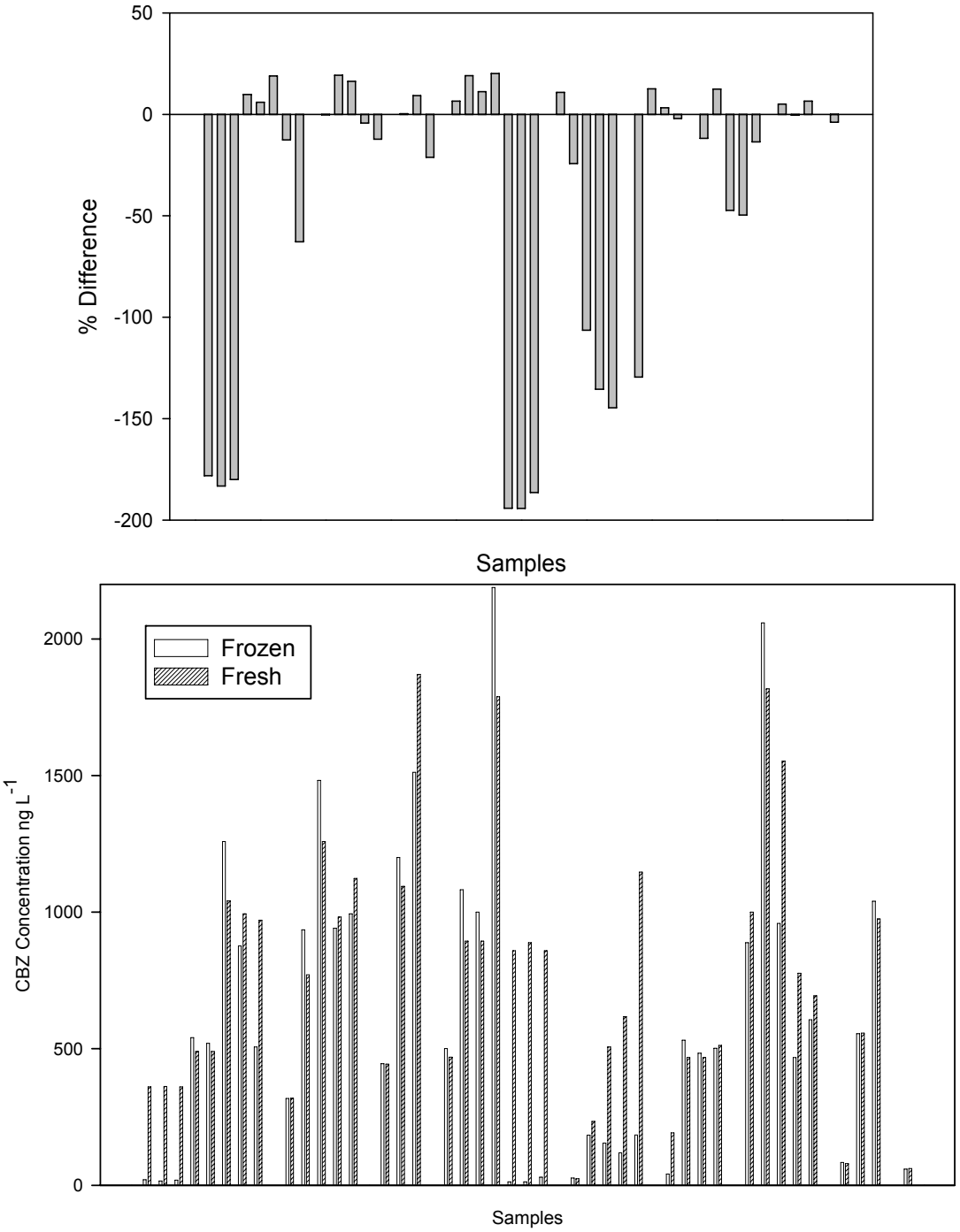


Figure B.2 – Percent difference in carbamazepine concentrations is plotted for all samples analyzed between a sample processed after collected (fresh), and a sample frozen, thawed, filtered and then processed (frozen). There are several bars with a very high per cent difference, many of which were run in duplicate or triplicate. A positive percent difference indicates that the frozen sample had a higher concentration than the fresh sample. The second plot illustrates the concentrations range for each sample, comparing the concentrations determined for the fresh sample versus those determined for the frozen sample.

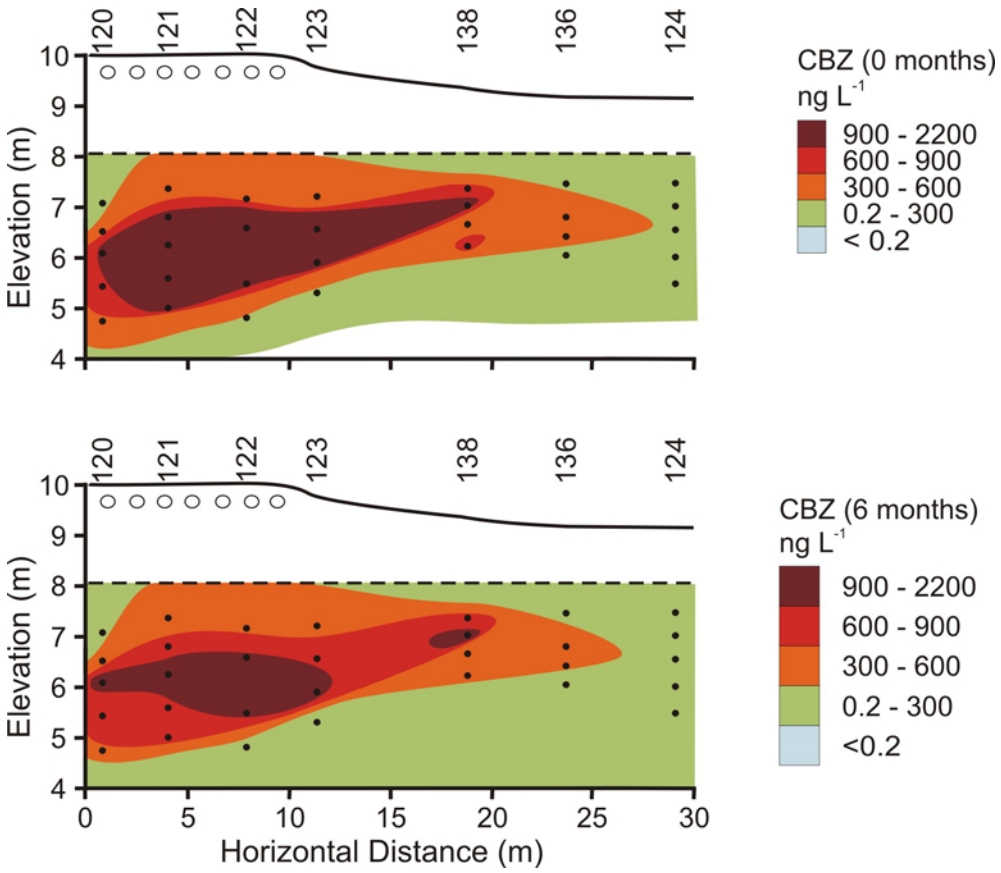


Figure B.3 – Plume delineations for carbamazepine (CBZ) for the same sample being analyzed immediately after SPE (0 months) and after storing solid phase extraction (SPE) eluate at 4°C for a period of 6 months (6 months). There is no substantial difference between the plume delineations when interpreting the plumes visually.

APPENDIX C: LONG POINT GEOCHEMICAL RESULTS

SAMPLE ID		Cl	NO_3	NO_3	SO_4	PO_4	NH_3/NH_4
		mg L^{-1}	*mg L^{-1}*	*as N mg L^{-1}*	*mg L^{-1}*	*as P mg L^{-1}*	*as N mg L^{-1}*
LP-124	1.6	7.60	3.17	0.72	39.8	0.008	< 0.1
	2.1	5.00	8.41	1.90	14.4	<0.005	< 0.1
	2.6	33.0	156.0	35.2	29.4	<0.005	< 0.1
	2.6D	32.5	152.9	34.6	31.0	<0.005	< 0.1
	3.1	54.1	250.1	56.5	40.1	<0.005	< 0.1
	3.6	41.4	183.9	41.6	61.5	<0.005	< 0.1
LP-136	1.9	45.0	270.8	61.2	29.6	1.07	0.1
	2.3	2.34	0.61	0.14	5.69	<0.005	< 0.1
	2.7	2.35	0.78	0.18	5.30	<0.005	< 0.1
	2.7D	2.33	0.82	0.18	5.33	<0.005	< 0.1
	3.1	19.9	70.6	15.9	14.0	<0.005	< 0.1
LP-138	1.9	43.4	293.9	66.4	31.7	3.680	< 0.1
	2.3	55.9	357.8	80.8	34.1	6.26	3.4
	2.3D	55.6	357.5	80.8	31.1	6.36	3.4
	2.7	56.1	277.3	62.7	32.8	0.014	< 0.1
	3.1	51.1	232.7	52.6	48.8	<0.005	< 0.1
LP-123	2.6	62.8	294.1	66.5	28.3	8.10	< 0.1
	3.2	48.4	341.7	77.2	35.5	7.33	< 0.1
	3.8	56.6	336.4	76.0	29.0	4.70	11.6
	4.5	45.3	261.3	59.0	37.6	<0.005	< 0.1
	4.5D	47.9	263.0	59.4	36.9	0.109	< 0.1
LP 122	2.8	59.8	326.6	73.8	78.9	7.63	< 0.1
	3.4	54.3	354.1	80.0	42.4	3.89	< 0.1
	4.6	51.2	270.1	61.0	36.6	0.847	1.7
	5.2	54.4	168.1	38.0	49.7	<0.005	< 0.1
LP-120	2.8	59.5	363.9	82.2	24.1	2.58	< 0.1
	2.9	61.2	369.6	83.5	24.7	2.62	< 0.1
	3.4	53.1	347.5	78.5	29.3	4.64	4.2
	3.9	52.4	253.7	57.3	39.2	0.977	0.8
	4.6	52.7	162.7	36.8	63.5	<0.005	0.7
	5.3	46.5	84.5	19.1	84.1	<0.005	0.2
LP-121	2.6	58.9	434.9	98.3	75.3	5.79	0.8
	3.2	59.1	326.5	73.8	39.9	3.94	3.0
	3.8	53.4	348.4	78.7	39.0	1.28	2.4
	4.4	52.2	271.3	61.3	30.3	0.126	1.9
	5	49.4	186.3	42.1	43.1	<0.005	0.3
LP Tank		64.2	-		31.5	16.03	148

a - Data obtained from Will Robertson October 4, 2006. All other reported data was obtained September 19, 2007

Duplicates are denoted by "D"

'-' denotes sample not processed

		2006 Field Data[a]			
SAMPLE ID		Mn *mg L^{-1}*	NO_3-N *mg L^{-1}*	NO_3^- *mg L^{-1}*	Cl *mg L^{-1}*
LP-124	1.6	0.00	9	40	6
	2.1	0.38	13	58	9
	2.6	0.30	23	102	21
	2.6D	0.29	-	-	-
	3.1	0.11	33	146	31
	3.6	0.15	18	80	30
LP-136	1.9	0.02	50	221	42
	2.3	0.27	67	297	57
	2.7	0.27	68	301	55
	2.7D	0.27	-	-	-
	3.1	0.38	57	252	32
LP-138	1.9	0.00	71	314	58
	2.3	0.18	-	-	-
	2.3D	0.18	72	319	59
	2.7	0.12	69	305	51
	3.1	0.60	62	274	53
LP-123	2.6	0.01	84	372	55
	3.2	0.03	68	301	59
	3.8	-	61	270	56
	4.5	0.15	24	106	36
	4.5D	0.15	-	-	-
LP 122	2.8	0.00			
	3.4	-			
	4.6	0.64			
	5.2	0.17			
LP-120	2.8	0.36			
	2.9	0.29			
	3.4	0.57			
	3.9	0.19			
	4.6	1.61			
	5.3	0.19			
LP-121	2.6	-			
	3.2	0.64			
	3.8	0.23			
	4.4	-			
	5	0.3			
LP Tank		-			

a - Data obtained from Will Robertson October 4, 2006. All other reported data was obtained September 19, 2007

Duplicates are denoted by "D"

'-' denotes sample not processed

APPENDIX D: CAMBRIDGE LANDFILL GEOCHEMICAL RESULTS

Well ID	Temperature	pH	Corrected Eh	F	Cl
	°C		*mV*	*mg L^{-1}*	*mg L^{-1}*
CL 10A	]	7.79	440	< 0.08	8.3
CL 51B	15.5	7.63	390	< 0.08	9.1
CL 51A	15	7.3	120	< 0.08	4.6
CL 52B	13	6.55	110	< 0.08	224.0
CL 53A	9.8	7.16	220	0.63	3.6
CL 25A	10.2	6.72	90	< 0.08	152.1
CL 25B	10.8	7.74	450	< 0.08	77.5
CL 25C	8.2	7.28	470	< 0.08	5.1
CL 53C	9.1	n/a	n/a	< 0.08	4.8
CL 53B	10	7.92	460	< 0.08	2.18
CL 52A	10	6.82	40	< 0.08	98.4
CL 10	12	6.77	220	< 0.08	77.3
CL 9B	18	6.45	20	< 0.08	34.6
B102	13	6.64	190	< 0.08	507.8
CL 47B	11.5	7.49	160	< 0.08	-
CL 47D				< 0.08	-
CL 47C	11	6.85	500	< 0.08	66.07
CL 47A	11	7.15	280	< 0.08	-
CL 64B	11	6.58	200	< 0.08	400.2
CL 64C	13.5	6.6	160	< 0.08	69.1
A101	11	6.79	250	< 0.08	116.4
A102				< 0.08	116.6
CL 63B	10.5	7.34	390	< 0.08	84.6
CL 63C	10.1	7	420	< 0.08	34.2
CL 55C	11.4	7.1	510	< 0.08	652.3
CL 55B	10.8	7.34	190	< 0.08	58.9
CL 55D				< 0.08	651.0
CL 29	9.9	7.35	470	< 0.08	75.8
CL 9	11.3	7.58	140	0.28	4.69
CL 24B	11	7.22	450	< 0.08	8.22
CL 70	35.8	7.36	n/a	< 0.08	
CL 68	22.8	6.48	n/a	< 0.08	
CL 69	25.2	6.86	n/a	< 0.08	
CL 44B	13.2	6.47	n/a	< 0.08	

n/a or '-' denotes sample not analysed for parameter

CL 55 D is duplicate of CL 55 C
A102 is duplicate of A101
CL 47D is duplicate of CL 47B

Well ID	NO_3	NO_3 as N	SO_4	PO_4 as P	DOC	NH_3/NH_4 as N
	mg L^{-1}	*mg L^{-1}*	*mg L^{-1}*	*mg L^{-1}*	*mg L^{-1}*	*mg L^{-1}*
CL 10A	< 0.4	< 0.09	24.1	0.008	< 1	< 0.1
CL 51B	< 0.4	< 0.09	29.7	< 0.005	1.7	0.3
CL 51A	< 0.4	< 0.09	22.1	0.006	< 1	< 0.1
CL 52B	< 0.4	< 0.09	< 0.2	0.015	22.6	1.4
CL 53A	< 0.4	< 0.09	83.1	< 0.005	1.7	< 0.1
CL 25A	< 0.4	< 0.09	26.5	< 0.005	3.1	0.2
CL 25B	1.53	0.35	58.7	< 0.005	< 1	< 0.1
CL 25C	< 0.4	< 0.09	23.8	< 0.005	1.4	< 0.1
CL 53C	< 0.4	< 0.09	28.4	< 0.005	1.3	< 0.1
CL 53B	< 0.4	< 0.09	14.9	< 0.005	< 1	< 0.1
CL 52A	< 0.4	< 0.09	11.0	< 0.005	8.4	0.5
CL 10	< 0.4	< 0.09	< 0.2	< 0.005	4.3	< 0.1
CL 9B	< 0.4	< 0.09	12.2	< 0.005	5.6	< 0.1
B102	< 0.4	< 0.09	< 0.2	< 0.005	65.4	46.6
CL 47B	< 0.4	< 0.09	417.0	0.005	< 1	0.2
CL 47D	< 0.4	< 0.09	443.0	< 0.005	< 1	0.2
CL 47C	< 0.4	< 0.09	56.7	< 0.005	2.6	< 0.1
CL 47A	< 0.4	< 0.09	792.6	< 0.005	<1	0.2
CL 64B	< 0.4	< 0.09	< 0.2	0.011	32.5	11.6
CL 64C	< 0.4	< 0.09	< 0.2	0.080	18.2	1
A101	< 0.4	< 0.09	31.0	< 0.005	2.4	< 0.1
A102	< 0.4	< 0.09	31.5	< 0.005	2.8	< 0.1
CL 63B	< 0.4	< 0.09	23.9	< 0.005	< 1	< 0.1
CL 63C	< 0.4	< 0.09	21.4	< 0.005	< 1	< 0.1
CL 55C	< 0.4	< 0.09	39.5	< 0.005	< 1	< 0.1
CL 55B	< 0.4	< 0.09	27.5	< 0.005	< 1	< 0.1
CL 55D	< 0.4	< 0.09	53.4	< 0.005	< 1	0.1
CL 29	< 0.4	< 0.09	35.3	< 0.005	< 1	< 0.1
CL 9	< 0.4	< 0.09	24.2	0.005	< 1	< 0.1
CL 24B	< 0.4	< 0.09	24.9	< 0.005	< 1	< 0.1
CL 70	< 0.4	< 0.09	n/a	1.387	881	1550
CL 68	< 0.4	< 0.09	n/a	0.005	6.5	6.8
CL 69	< 0.4	< 0.09	n/a	1.722	103	1.8
CL 44B	< 0.4	< 0.09	n/a	0.005	11.9	19.5

CL 55 D is duplicate of CL 55 C
A102 is duplicate of A101
CL 47D is duplicate of CL 47B

n/a or '-' denotes sample not analysed for parameter

Well ID	CH_4	CH_4 (duplicate)	CH_4 Average:	Sample Volume	Alkalinity (with 1.6N H_2SO_4) Digits	Alkalinity
	mg L^{-1}	*mg L^{-1}*	*mg L^{-1}*	*(mL)*	*(to pH 4.5)*	*(mg L^{-1} Total $CaCO_3$)*
CL 10A	2.3	1.7	2.0	125	271	217
CL 51B	0.7	0.7	0.7	24.8	50	202
CL 51A	0.5	0.4	0.5	21.6	59	273
CL 52B	18.3	19.8	19.0	23.2	244	1052
CL 53A	< 0.2	< 0.2	< 0.2	24.4	75	307
CL 25A	10.0	9.0	9.5	24	187	779
CL 25B	< 0.2	< 0.2	< 0.2	22.8	83	364
CL 25C	< 0.2	< 0.2	< 0.2	24.3	74	305
CL 53C	1.5	1.5	1.5	23.4	87	372
CL 53B	< 0.2	< 0.2	< 0.2	24	48	200
CL 52A	9.3	8.1	8.7	24	156	650
CL 10	18.6	15.4	17.0	24.1	199	826
CL 9B	10.0	11.0	10.5	24.2	294	1215
B102	8.5	8.5	8.5	24.2	393	1624
CL 47B	< 0.2	< 0.2	< 0.2	22.6	52	230
CL 47D	< 0.2	< 0.2	< 0.2	22.6	52	230
CL 47C	0.4	0.4	0.4	21.4	122	570
CL 47A	< 0.2	< 0.2	< 0.2	23.5	84	357
CL 64B	9.0	8.9	9.0	23.6	277	1174
CL 64C	4.3	4.2	4.3	24.2	208	860
A101	1.7	1.6	1.7	22	116	527
A102	1.6	1.7	1.7	22	116	527
CL 63B	< 0.2	< 0.2	< 0.2	22.4	77	344
CL 63C	< 0.2	< 0.2	< 0.2	22	54	245
CL 55C	< 0.2	< 0.2	< 0.2	24.7	119	482
CL 55B	2.6	2.8	2.7	22.5	83	369
CL 55D	< 0.2	< 0.2	< 0.2			
CL 29	1.2	1.2	1.2	24.3	87	358
CL 9	0.7	0.7	0.7	24.6	63	256
CL 24B	< 0.2	< 0.2	< 0.2	24.8	90	363
CL 70	6.1	6.7	6.4	n/a	n/a	n/a
CL 68	8.4	8.1	8.2	n/a	n/a	n/a
CL 69	15.9	17.1	16.5	n/a	n/a	n/a
CL 44B	12.2	11.9	12.0	n/a	n/a	n/a

CL 55 D is duplicate of CL 55 C
A102 is duplicate of A101
CL 47D is duplicate of CL 47B

n/a or '-' denotes sample not analysed for parameter

APPENDIX E: WATERLOO LANDFILL GEOCHEMICAL RESULTS

Sample ID	pH	Corrected Eh	Cl	NO_3	NO_3 as N
		mV	*mg L^{-1}*	*mg L^{-1}*	*mg L^{-2}*
298 - 99	6.83	170	62.2	< 0.4	< 0.09
WW 9	8.34	240	2.7	< 0.4	< 0.09
8 - 83	8.09	40	26.8	< 0.4	< 0.09
334 - 03	6.5 - 7	n/a	164.4	< 0.4	< 0.09
316A - 01	6.5	270	4.5	< 0.4	< 0.09
324B - 02	6.41	330	18.2	< 0.4	< 0.09
7 - 83	6.97	120	58.3	< 0.4	< 0.09
320 - 02	6.25	140	11.6	< 0.4	< 0.09
77 - 89	7.07	120	14.4	< 0.4	< 0.09
318 - 01	6.64	220	15.2	< 0.4	< 0.09
318 - 08	n/a	n/a	15.2	< 0.4	< 0.09
164 - 92	7.37	120	30.2	< 0.4	< 0.09
84 - B	7.48	140	5.7	< 0.4	< 0.09
296A - 99	6.67	170	13. 4	< 0.4	< 0.09
308A - 01	7.42	100	11.0	< 0.4	< 0.09
308B - 01	6.05	180	7.8	< 0.4	< 0.09
309A - 01	7.59	210	3.4	< 0.4	< 0.09
309B - 01	7.18	190	12.0	< 0.4	< 0.09
310A - 01	7.48	100	3.7	< 0.4	< 0.09
312A - 01	7.46	380	n/a	n/a	n/a
312C - 01			5.1	0.62	0.14
312B - 01	7.28	370	4.3	0.51	0.12
315A - 01	7.53	150	14.5	< 0.4	< 0.09
317 - 01	6.95	150	49.3	< 0.4	< 0.09
321 - 03	7.31	140	9.6	< 0.4	< 0.09

312 A-01 and 312C-01 are duplicates
318-08 is a duplicate of 318-01

Sample ID	SO_4	PO_4 as P	DOC	NH_3/NH_4 as N	DO
	mg L^{-1}	*mg L^{-1}*	*mg L^{-1}*	*mg L^{-1}*	*mg L^{-1}*
298 - 99	50.0	0.008	12.5	< 0.1	2.5
WW 9	6.3	0.0140	< 1	0.2	0.2
8 - 83	51.1	0.005	2.5	< 0.1	0.8
334 - 03	< 0.2	0.185	116.0	24.0	1.0
316A - 01	25.4	0.015	11.5	< 0.1	0.9
324B - 02	23.7	0.014	2.8	< 0.1	1
7 - 83	< 0.2	0.017	55.3	0.1	0.2
320 - 02	56.1	0.019	1.1	< 0.1	0.4
77 - 89	39.0	0.018	1.3	< 0.1	0.3
318 - 01	49.7	0.015	4	0.1	2
318 - 08	49.6	0.016	3.7	0.1	n/a
164 - 92	47.4	0.017	< 1	< 0.1	0.8
84 - B	75.1	0.027	< 1	< 0.1	0.9
296A - 99	33.3	0.008	< 3	< 0.1	0.8
308A - 01	63.9	0.008	< 1	< 0.1	0.4
308B - 01	66.3	0.006	< 1	< 0.1	1
309A - 01	62.3	0.005	< 1	< 0.1	0.9
309B - 01	54.0	< 0.005	< 1	< 0.1	0.6
310A - 01	52.9	0.008	< 1	< 0.1	0.3
312A - 01	n/a	< 0.005	< 1	< 0.1	0.6
312C - 01	60.4	0.007	< 1	< 0.1	n/a
312B - 01	67.7	0.008	< 1	< 0.1	0.9
315A - 01	24.1	0.007	< 1	< 0.1	3
317 - 01	26.1	0.019	4.4	1.9	3
321 - 03	55.6	0.009	< 1	< 0.1	0.4

312 A-01 and 312C-01 are duplicates
318-08 is a duplicate of 318-01

Sample ID	Dissolved CH_4	CH_4 (Duplicate)	CH_4 Average:	Volume	Alkalinity Digits	Alkalinity
	mg L^{-1}	*mg L^{-1}*	*mg L^{-1}*	*mL*	*(to pH 4.5)*	*mg L^{-1} as $CaCO_3$*
298 - 99	3.8	4.6	4.2	24	125	521
WW 9	< 0.2	0.2	0.1	24.4	34	139
8 - 83	< 0.2	n/a	< 0.2	21.2	55	259
334 - 03	4.9	4.8	4.8	24.8	234	943.5
316A - 01	0.8	1.6	1.2	23.9	236	987
324B - 02	7.9	6.9	7.4	22.4	179	799
7 - 83	n/a	8.5	8.5	24	145	604
320 - 02	1.3	1.2	1.2	23.4	75	321
77 - 89	3.2	2.7	3.0	24	99	413
318 - 01	17.8	21.1	19.5	24.6	98	398
318 - 08	20.9	24.4	22.6	n/a	n/a	n/a
164 - 92	0.6	0.5	0.5	24	71	296
84 - B	< 0.2	< 0.2	< 0.2	24.2	77	318
296A - 99	7.0	7.5	7.3	24.6	187	760
308A - 01	< 0.2	< 0.2	< 0.2	24.7	65	263
308B - 01	n/a	n/a	n/a	23.5	103	438
309A - 01	< 0.2	< 0.2	< 0.2	22.6	67	297
309B - 01	2.4	2.2	2.3	24.7	100	405
310A - 01	< 0.2	< 0.2	< 0.2	24.2	63	260
312A - 01	0.6	0.6	0.6	24.8	75	302
312C - 01	n/a	0.8	0.8	n/a	n/a	n/a
312B - 01	0.5	0.5	0.5	23.5	83	353
315A - 01	0.7	0.7	0.7	24.9	72	289
317 - 01	1.1	0.9	1.0	22.3	77	345
321 - 03	1.0	1.0	1.0	22.5	80	356

312 A-01 and 312C-01 are duplicates
318-08 is a duplicate of 318-01