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PARTITIONING OF CHEMICALS OF CONCERN TO COLLOIDAL ORGANIC MATTER IN MUNICIPAL WASTEWATER

by

KERRY NEIL MCPHEDRAN

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Partitioning of chemicals of concern to colloidal organic matter in municipal wastewater

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ABSTRACT

Fate and transport of chemicals of environmental concern throughout municipal wastewater treatment plants (MWTPs) affect the safety of human and environmental health. Understanding of the fate of historic and emerging contaminants in MWTPs allows for consideration and prediction of potential environmental loadings and subsequent risk assessment. The aim of this thesis was to develop a robust and reproducible method to discern partitioning of a suite of chlorobenzenes (CBs) to well-characterized colloidal organic carbon (COC) of MWTP raw influents.

Preliminary investigations support the use of MeOH cosolvent at volume fractions up to 1%. Given that cosolvent may also interact with COC directly, a 0.01% MeOH volume fraction was used in all studies. Henry's law constants (HLCs) used to determine the partitioning coefficient must be accurate and exhibit marked variability in the literature, thus calculating experiment-specific HLCs was needed. HLCs determined for the CBs ranged from 29.9–56.5 Pa m^3 mol^{-1}. Ultrafiltration fractionation was used to separate colloidal fractions followed by various techniques to characterize the COC. The major finding of size fractionation was the abundance of mass under the 1 kDa size fraction (ca. 70%). Sample preparation and liquid-state ^{1}H NMR has not been previously used and serves as a valuable evolution for sample processing and COC characterization

The partitioning of CBs to MWTP colloids under 1.5 μm resulted in $\log K_{COC}$ values of 3.86, 3.89, and 3.19 for TeCB, PeCB, and HCB, respectively; these values did not follow trends based upon hydrophobicity. Contrary to expectations based on literature investigations COC under 1 kDa participated in partitioning with $\log K_{COC}$ values of 4.30, 4.36, and 3.74 for TeCB, PeCB, and HCB, respectively.

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CHAPTER 1

General Introduction

1. Introduction

Water is critical for all aspects of human and ecosystem health. Water supply is finite, thus consideration of wastewater impact on receiving environments which are used as reservoirs for drinking water and other uses must be made prior to release. Water is constantly recycled throughout the environment, however, many locations have inadequate supply of fresh waters due to human impacts on both the quantity (eg. water taken for agricultural use) and quality (eg. chemical contamination). Human impacts via wastewaters on water quality must be considered to protect sources both for now and for the future.

Wastewater treatment is employed for waters collected from residential, commercial, and industrial sources which will be returned as environmental loadings via effluents and sludges or be destined for reuse in the face of declining freshwater resources. As populations inevitably grow total discharges from all wastewater sources increase, therefore treatment must be extensive enough to ensure protection of both human and environmental health. Historically treatment has only considered reduction in organic matter and pathogens. More recently the additional goal of treating chemicals of concern (CHCs) has become of interest. As water is cycled throughout the environment broad treatment of wastewater prior to release is essential.

Treatment of wastewater has customarily been defined via nonspecific factors such as biochemical oxygen demand (BOD) and suspended solids (SS) (Levine et al., 1985). These nonspecific factors do not consider treatability of all organic constituents found in wastewater (Fig. 1). Additionally, treatment of chemical compounds both of historic and emerging concern (Table 1) has not been traditionally considered in treatment

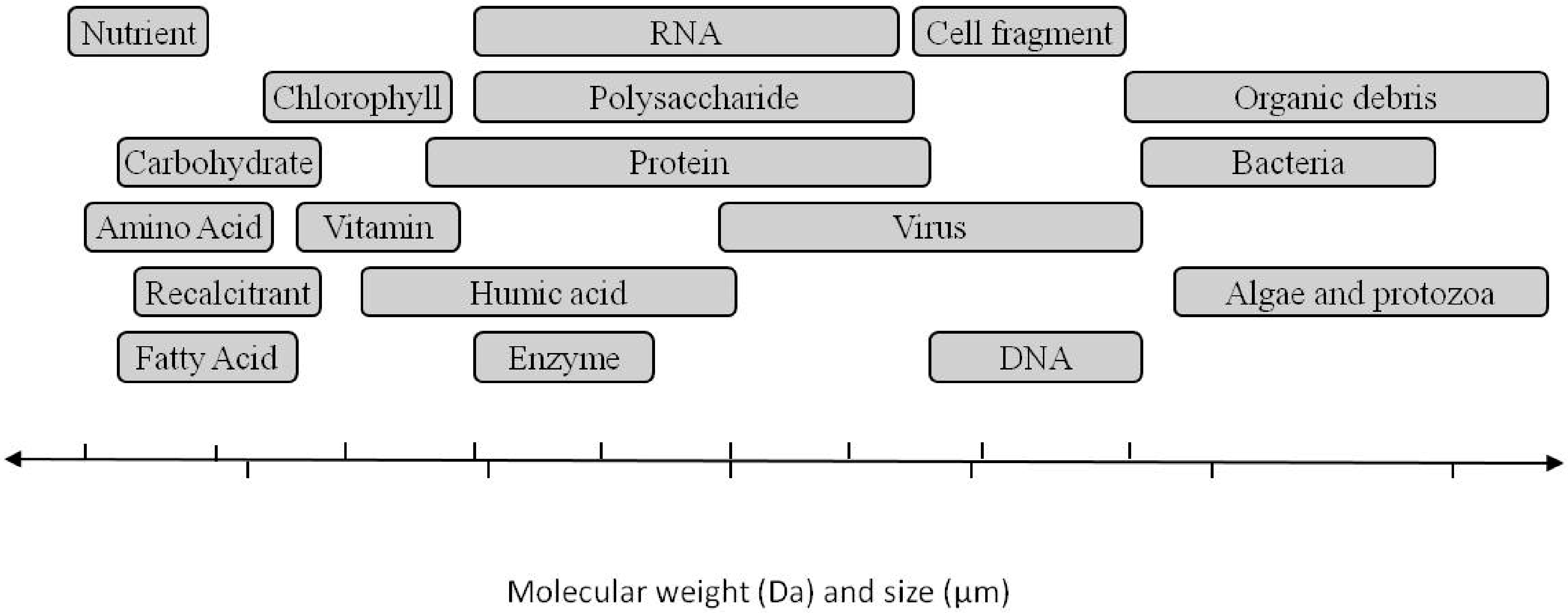

Fig. 1: Typical organic constituents in a WWTP process including size ranges and historic and current colloids size distinctions. Adapted from Levine et al. (1985) and Shon et al. (2006)

Table 1: Classes of potential MWTP chemical compounds. Adapted from Hannah et al. (1985) and Barceló (2003).

Group	Examples
Volatile organics	dichloroethane, bromoform, chloroform, ethylbenzene
Phenolics	Pentachlorophenol, phenol
PAHs	Napthalene, pyrene, phenanthrene, fluoranthene
Phthalates	DEHP, DBP
Pesticides	Heptachlor, isophorone, lindane
Chlorobenzenes	Dichlorobenzene, tetrachlorobenzene, pentachlorobenzene, hexachlorobenzene
Pharmaceuticals	
Veterinary and human antibiotics	Trimethoprim, erythromycin, lincomycin, sulfamethoxazole
Analgesics and anti-inflammatory drugs	Codeine, ibuprofen, acetaminophen, acetylsalicylic acid, diclofenac, fenoprofen
Psychiatric drugs	Diazepam
Lipid regulators	Bezafibrate, clofibric acid, fenofibric acid
b-blockers	Metoprolol, propranolol, imolol
X-ray contrast media	Iopromide, iopamidol, diatrizoate
Steroids and hormones (contraceptives)	Estradiol, estrone, estriol, diethylstilbestrol
Personal care products	
Fragrances	Nitro, polycyclic and macrocyclic musks
Sun-screen agents	Benzophenone, methylbenzylidene camphor
Insect repellents	N,N-diethyltoluamide
Antiseptics	Triclosan, chlorophene
Surfactants and surfactant metabolites	Alkylphenol ethoxylates, alkylphenols (nonylphenol and octylphenol), alkylphenol carboxylates
Flame retardants	Polybrominated diphenyl ethers (PBDEs), Tetrabromo bisphenol A, Tris(2-chloroethyl)phosphate
Industrial additives and agents	Chelating agents (EDTA), aromatic sulfonates
Gasoline additives	Dialkyl ethers, Methyl-t-butyl ether (MTBE)
Disinfection by-products	Iodo-THMs, bromoacids, bromoacetonitriles, bromoaldehydes, cyanoformaldehyde, bromate, NDMA

plant design (Shon et al., 2006). Overall, the treatability of wastewater organic matter (OM) has shown to be dependent on size distributions (Levine et al., 1985), while the treatability of CHCs in wastewater has not been extensively studied.

Extensive research on natural organic matter (NOM) in surface waters has been performed, including the potential role of partitioning of CHCs to NOM in chemical fate and transport (Backhus et al., 1990; Gustafsson et al., 1997; Laor and Rebhun, 2002; Shon et al., 2006). Despite the extent and importance of this CHC–NOM relationship, few studies have considered wastewater CHC–OM partitioning (Holbrook et al., 2004).

The OM of particular interest in wastewater are colloids, defined as particles ‘immune to gravity’ (Graham, 1861). These colloids have the ability to sorb CHCs, thus rendering CHCs inaccessible to degradation and other loss processes (Gustafsson et al., 1997). Freely-dissolved (unbound chemical) and colloid-bound CHCs can be readily transported via effluents into receiving waterbodies where they may negatively impact both humans and the general environment.

1.1.Wastewater treatment processes

Municipal wastewater treatment plants (MWTPs) treatment objectives have developed markedly from about 1900 to present day. Original treatment objectives involved removal of organic matter, treatment of biodegradable organics, and elimination of pathogens (Tchobanoglous et al., 2001). By the early 1980s these objectives became more stringent and necessitated the removal of nutrients including nitrogen and phosphorus which were found to be negatively affecting surface waters (Tchobanoglous et al., 2001).

To meet these objective MWTPs use physical, chemical, and biological processes in various “reactors” (Tchobanoglous et al., 2001) including batch, completely-mixed, plug-flow, packed-bed, and fluidized bed. These reactors are used in various configurations for primary, secondary, and tertiary treatment processes. Primary treatment or primary sedimentation is a treatment process used to remove SS and the associated BOD. Secondary treatments are used to substantially degrade the remaining organics via fixed-film processes (eg. trickling filters and rotating biological contactors) and suspended-growth processes (eg. activated sludge and lagoons). Tertiary treatments or ‘polishing’ generally is a disinfection process (eg. chlorination, UV, and ozonation) that may be considered depending on effluent quality.

Overall, these objectives are well met by use of an activated sludge-type treatment plant (Fig. 2). This plant design includes physical, chemical, and biological treatment processes through preliminary grit removal, a primary settling tank, an aeration tank, and a secondary settling tank. A tertiary advanced treatment process may also be included dependent on effluent parameters.

Of current interest is specifically the primary treatment tank process (Fig. 2). The primary tank volatilization and degradation are limited for many CHCs, including hydrophobic organic compounds (HOCs). These HOCs have a high affinity for both solids and colloids. Freely-dissolved and CHC–colloid chemicals are transferred to the aeration tank via primary effluents. The CHC–colloid complexes render the chemical unavailable for degradation processes (Gustafsson et al., 1997). These colloids do not settle readily and act to transport CHCs to the environment via MWTP effluents.

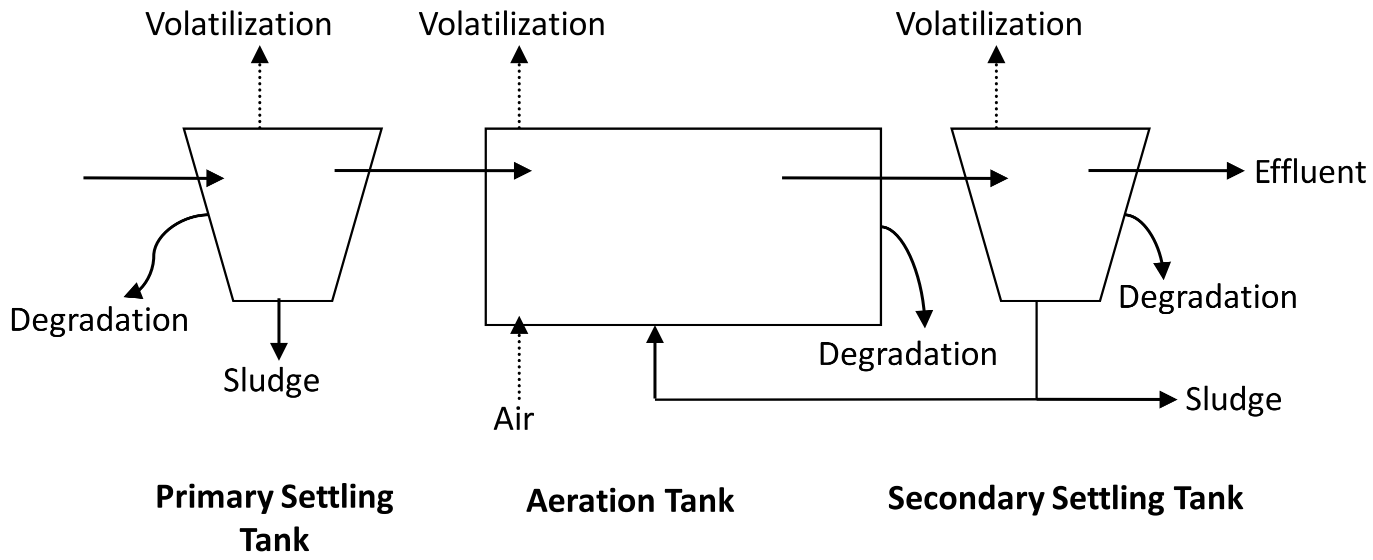

Fig. 2: Schematic of a typical activated sludge wastewater treatment plant (WWTP) with chemical fate and transport processes.

1.2.Wastewater organic constituents

Wastewater organics constituents are shown in Fig. 1 which vary widely in physicochemical characteristics (Müller et al., 2000; Her et al., 2002; Leenheer et al., 2003). Knowing these characteristics is invaluable in optimization of MWTP processes (Shon et al., 2006). The most valuable characterization is size distribution which affects rates of sedimentation, mass transfer, adsorption, diffusion, and biochemical reactions (Levine et al., 1985). Size distributions have been reported for various MWTP processes (Manka et al., 1982; Vaillant et al., 1999; Holbrook et al., 2004; Sophonsiri et al. 2004). Unfortunately, a standard method of size fractionation has not been considered for MWTP samples making use and comparison of literature values difficult.

Of particular interest is the distinction between suspended solids, colloids, and truly-dissolved (colloids unable to bind specific CHCs) since functional separation of these phases unclear in the literature. Values chosen for lower cut-off of suspended solids or particulate organic carbon range from 0.45 – 1.5 µm (Tchobanoglous et al., 2001; Vaillant et al., 1999; Holbrook et al., 2004; Shon et al., 2006), while those chosen for upper cut-off for the truly-dissolved phase filter range from 500 – 1000 Da (Backhus et al., 1990; Gustafsson et al., 2001; Backhus et al., 2003; Holbrook et al., 2004). The assignment of phases based primarily on filter sizes rather than actual OM physicochemical characteristics has been used extensively in the literature. These arbitrary assignments of phases make the distinction of chemical sorption behaviour difficult to assess since they have no operational or functional basis.

1.3. Organics size characterization

Many analytical techniques are available to identify size fractions of MWTP organic constituents (Fig. 3). With comparison of Fig. 1, it is apparent that many of the techniques are not able to detect all of the potential organic constituents. Of special interest recently are the smallest size fractions, which could not be readily identified before advanced fractionation methods were introduced. These include ultrafiltration, high pressure liquid chromatography, gel filtration chromatography, and flow field flow fractionation (Fig. 3). The ultrafiltration method is particularly attractive since it allows separation of size fractions without sacrificing samples, allowing further characterization of the fractionated sample. Additionally, when coupled with traditional membrane filtration methods this technique covers the entire organic constituent size ranges, thus allowing a single-type of technique to be used exclusively for size characterization of samples.

1.4.Chemicals of concern

Prior to the 1990s, U.S. Environmental Protection Agency priority pollutants were the focus of environmental concern for wastewater effluent (Shon et al., 2006). These historic chemicals include the first six groups listed in Table 1. These groups include HOCs such as the chlorobenzenes that are persistent in the environment. The emerging chemical groups include the remaining nine groups listed in Table 1, including HOCs such as synthetic musks, polybrominated diphenyl ethers, and alkylphenols which have received little attention in effluents (Halling-Sørenson et al., 1998; Shon et al., 2006).

Fate and transport of both historic and emerging chemicals through the MWTP process is important in elucidation of environmental loadings. Partitioning of these

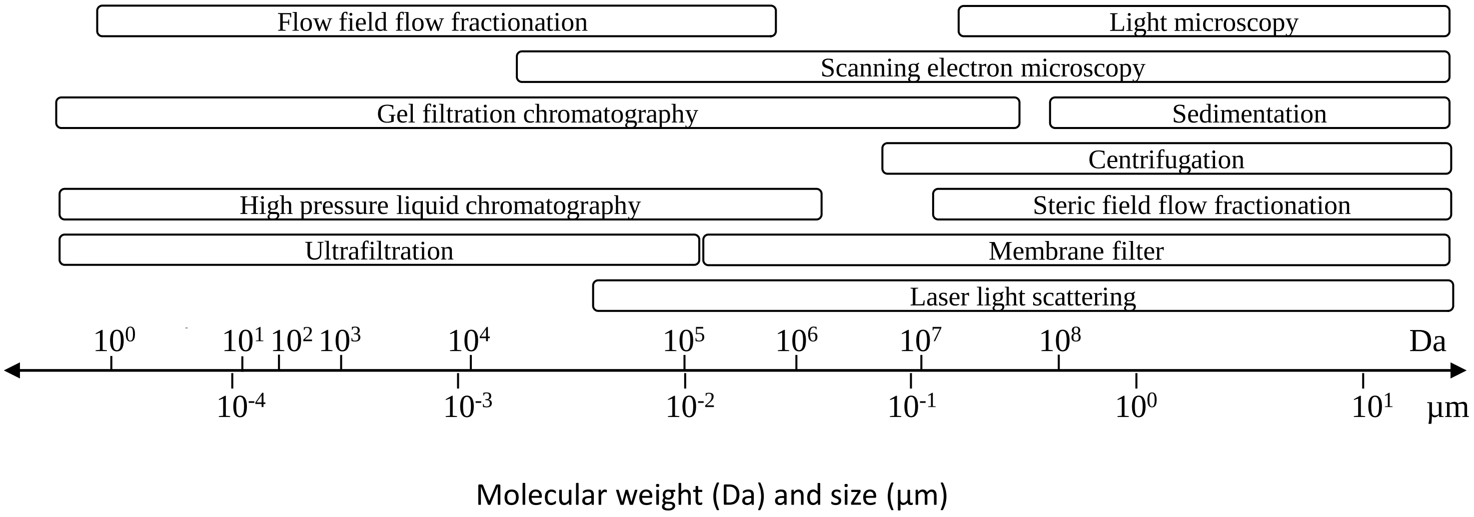

Fig. 3: Analytical techniques used to indentify organic matter size ranges. Adapted from Levine et al. (1985) and Shon et al. (2006).

chemicals to colloids during the MWTP has not been considered extensively, despite the potential importance of the CHC–colloid relationship. Given the availability of well-defined physicochemical properties of HOCs, such as chlorobenzenes, they are an excellent chemical class to consider for partitioning experiments to better understand and quantify the importance of the CHC–colloid relationship.

1.5.Chlorobenzenes

The chlorobenzenes (CBs) are a diverse suite of chemicals with a well-defined set of physicochemical properties. Currently, CBs are not known to be manufactured for any commercial uses (Wang et al., 1998; Barber et al., 2005; Bailey et al., 2009). Historically, only hexachlorobenzene (HCB) was used directly in industry and agriculture as a fungicide (Barber et al., 2005). The remaining CBs (including HCB) were added as a chlorobenzene mixture to reduce the viscosity of PCB products employed for heat transfer (King et al., 2003) or as intermediates in process solvents in the manufacture of pesticides and chlorinated phenols (Wang et al., 1998). Despite no longer being manufactured, all the chlorobenzenes are still being continually released into the environment via byproduct emissions, pesticide use, combustion processes, and degradation from dechlorination of other chlorobenzenes (Bailey et al., 2009).

1.6.Organic compound sorption: Chemcentric viewpoint

The partitioning of CHCs to OM is dependent on the affinity of the chemical to the OM. This interaction is based on both the nature of the sorbent (OM) and the physicochemical properties of the sorbate (CHC) (Delle Site, 2001). These interactions are grouped into physical, chemical and electrostatic. These groups can be further divided into van der Waals forces, hydrophobic bonding, hydrogen bonding, charge transfer, ligand-exchange and ion binding, ion-dipole and dipole-dipole, and covalent bonds (Weber et al., 1991). These interactions are difficult or impossible to measure individually and/or directly, thus indirect sorption affinity can be found via a partitioning coefficient that can be determined experimentally. This partitioning coefficient may be further investigated via characterization of OM and physicochemical properties of CHC and serves as an overall summation of the interactions mentioned previously.

To investigate the potential partitioning behaviour a functional definition of colloids is needed to separate the 'truly-dissolved' (unable to bind CHCs) from the colloidal (able to bind CHCs) OM fractions. In conjunction with the truly-dissolved definition, 'freely-dissolved' chemical is unbound to any OM making it accessible for potential loss processes. Historically the separation of these fractions was based solely on filterable versus non-filterable segments which do not behave according to interactions mentioned above. For aquatic colloids Gustafsson and Gschwend (1997) introduced a 'chemcentric' sorption regime which includes a more operationally defined OM distinction based on chemical properties. Currently, the lower cut-off for the colloid and truly-dissolved is debatable. Previously, a range of 500 Da – 1 kDa has been considered acceptable for defining the truly-dissolved fraction for aquatic colloids based on the limit of current membrane size fractionation (Backhus et al., 1990; Gustafsson and Gschwend, 1997; Gustafsson et al., 2001; Backhus et al., 2003). Recently, Holbrook et al. (2004) have used a 1 kDa size as the cut-off to define truly-dissolved organic matter in a study related to MWTP colloids. However the validity of a 1 kDa cut-off size is untested. In the current study, the colloidal fraction is considered to be passing 1.5 µm and the truly-dissolved passing 1 kDa a reasonable starting point for the chemcentric theory (Fig. 4).

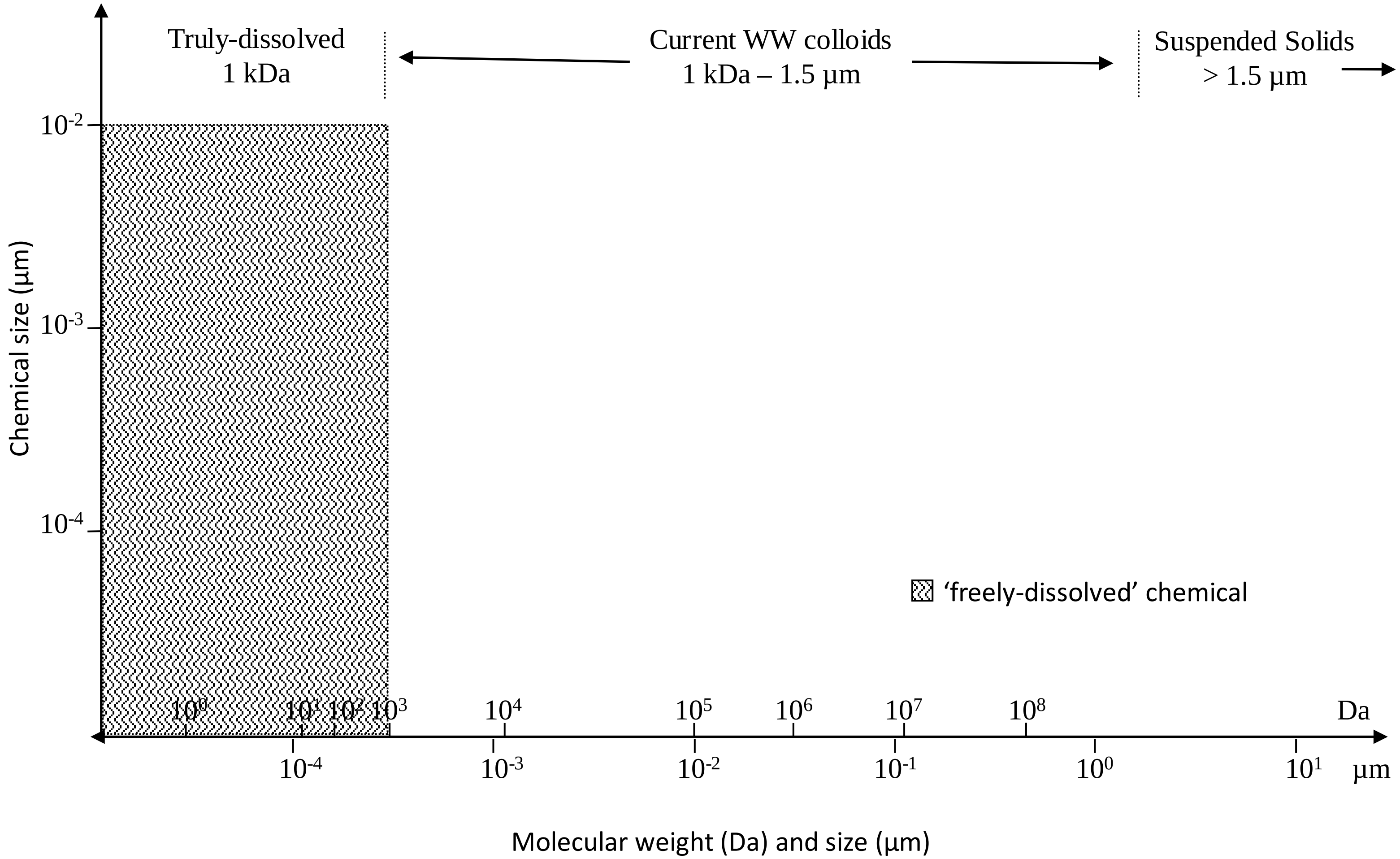

Fig. 4 : Chemical size vs. organic size (and weight) indicative of potential partitioning ability. Identification of dissolved, colloidal and suspended soils considered in the current study.

2. Thesis Objective

The main objective of this thesis was to investigate and quantify HOC partitioning to colloidal organic matter in municipal wastewater. A suite of three chlorobenzenes (1,2,4,5-tetrachlorobenzene, pentachlorobenzene, hexachlorobenzene) was chosen and their partitioning to colloidal organic matter in primary effluent of Little River Pollution Control Plant was examined. In standard methods of wastewater analyses a 1.5 µm filter is used to define the lower limit of suspended solids. This size was used to define the upper limit of colloidal organic matter in the current study.

2.1.Chapter 2

Partitioning of CBs to colloids has been investigated via spiking of CBs in the cosolvent methanol (MeOH) into samples containing MWTP OM. This cosolvent may impact both the solution phase as well as the OM directly (Bouchard, 2003). Solid-phase microextraction (SPME) is a relatively new technique for determination of CHC partitioning in soils, sediments, and waterbodies (Potter et al., 1994; Artola-Garicano et al., 2003; Bruheim et al., 2003; Fernández-González et al., 2007). HS-SPME is a modification of the technique which allows the sampling of the headspace (HS) which provides a direct measurement of vapour phase chemical concentrations.

The goal of the Chapter 2 study is to determine the effects of experimentally relevant volume fractions (f_c) of the cosolvent MeOH on apparent solubility of chlorobenzenes. These experiments used HS-SPME methods for batch studies using three chlorobenzenes (1,2,4,5-tetrachlorobenzene, pentachlorobenzene, hexachlorobenzene). Further experiments include assessment of chemical stability over time in raw glass and silanized SPME headspace vials. The results of these experiments will be considered in cosolvent behaviour for future MWTP partitioning research.

2.2.Chapter 3

Henry's law constant (H) is a parameter which may be used to describe mass transfer between water and air which is important for use in environmental risk assessment and fate and transport models (ten Hulscher et al., 2006). Accurate determination of H is needed, unfortunately, the quality of measured physicochemical data including H has been recently questioned (Goss et al., 2004; ten Hulscher et al., 2006). Accurate determination is needed to avoid misinterpretation and erroneous conclusions based upon incorrect parameters (Goss et al., 2004).

The goal of the Chapter 3 is to establish H values for the three CBs using the gas sparging technique. Given large variations in literature H values, determination of experiment-specific values is valuable in future use of gas sparging in the determination of partitioning behaviour in MWTP processes.

2.3.Chapter 4

Treatability of wastewater is strongly dependent on OM size distributions. Characterization of OM sizes is needed for both understanding of processes and in selection of potential treatment techniques (Levine et al., 1985). After size distributions are determined, further characterization techniques can be used to correlate partitioning of CHCs to OM fractions. Ultrafiltration is the only technique in which MWTP samples can be fractionated without sacrificing, allowing further characterization. When coupled with membrane filtration, these two filtration techniques allow for determination of the entire MWTP OM distribution.

Objectives of Chapter 4 are to develop a repeatable and robust size fractionation method for MWTP primary effluents which allows for further characterization of fractionated OM. The overall goal is to increase the understanding of OM distribution and characteristics and partitioning of CHCs to various size fractions. With this information fate and transport of CHCs may be determined via use of partitioning parameter. For comparative purposes, Aldrich humic acid (AHA) samples were also characterized to determine their applicability as a standard reference for technique verification.

2.4.Chapter 5

CHCs in wastewater are a concern due to potential for environmental and human health risks. Movement of these pollutants, bound or freely-dissolved, throughout the MWTP process is not well understood. The term K_{COC} is used to define partitioning between water and colloidal organic carbon (COC; organic matter normalized by its carbon content). Evaluation of CHC – COC sorption is especially needed for primary sedimentation effluents since bound CHCs are not removed via degradation pathways, volatilization, and/or sedimentation during secondary treatment, thereby released to natural systems via effluents into receiving water bodies (Holbrook et al., 2004).

In Chapter 5, the sorption of three chlorobenzenes (1,2,4,5-tetrachlorobenzene, pentachlorobenzene, and hexachlorobenzene) to two organic matter sources (MWTP derived COC and Aldrich humic acids – AHA) is investigated. The objectives of this study are (1) quantify K_{COC} for the MWTP primary tank effluent; (2) quantify K_{COC} of

AHA for comparison to historic values and methodology confirmation; (3) determine rate constants of partitioning for both effluents and AHA; (4) determine the potential interactions between the mix of chlorobenzenes with COC.

2.5.Chapter 6

A limitation to the determination of the truly-dissolved COC fraction has been the inability to separate COC experimentally. Recently, the ultrafiltration technique has become widely used in isolation of both environmental (Wilding et al., 2004; Kottelat et al., 2008; Maskaoui et al., 2010) and MWTP colloids (Holbrook et al., 2004; Worms et al., 2010). Ultrafiltration allows isolation of COC down to 1 kDa, which has been considered as the lower limit to OM colloidal matter (Gustafsson et al., 1997; Holbrook et al., 2004).

The objective of the Chapter 6 is to determine if the 1 kDa limit to COC partitioning is valid. Using the gas sparging technique, and various size fractions of organics for comparison, spiked chlorobenzene partitioning is investigated using the primary effluent of a MWTP which is chosen since CHCs partitioned to COC are not readily accessible for volatilization and degradation in the secondary MWTP treatment and may be carried to receiving environments through final MWTP effluents.

2.6.Chapter 7

The importance of determination of the fate and transport of CHCs throughout MWTP processes are of utmost concern for the safety of both human and environmental health. The primary treatment process of the MWTP is crucial in determining the partitioning of CHCs to OM which affects transport processes. The partitioning behaviour can be better understood through the use of a chemcentric framework that is developed within this Chapter.

The objective of Chapter 7 is to integrate results of the previous experimental chapters and discuss the implications of the research in the MWTP process. After developing the framework for partitioning experiments, Chapter 7 outlines the relevance of primary wastewater treatment and the chemcentric viewpoint. Chapter 7 will include overall conclusions of the thesis and relevant engineering significance.

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CHAPTER 2

Investigation of chlorobenzene (1,2,4,5-tetrachlorobenzene, pentachlorobenzene, hexachlorobenzene) partitioning with cosolvent methanol and disappearance pathways using solid-phase microextraction

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1. Introduction

Determination of hydrophobic organic compound (HOC) sorption to colloidal organic carbon (COC; organic matter categorized by carbon content) in municipal wastewater treatment plants (MWTP) and natural organic matter (NOM) in soils, sediments, and waterbodies is crucial for understanding chemical fate including transport, degradation, volatilization, and biological accessibility. Historically, partitioning of HOC sorption to DOM/NOM has been investigated via spiking of HOCs in methanol (MeOH) into experimentally prepared samples containing organic material. This method of spiking leads to addition of a cosolvent phase (MeOH) in addition to the HOC; this cosolvent may impact both the solution phase as well as the DOM/NOM directly, thus potentially affecting partitioning properties of HOCs (Bouchard, 2003).

Solid-phase microextraction (SPME) is a relatively new technique for determination of HOC partitioning behaviour in soils, sediments, and waterbodies (Potter et al., 1994; Langenfeld et al., 1996; Porschmann et al., 1998; Ramos et al., 1998; Artola-Garicano et al., 2003; Bruheim et al., 2003; Fernández-González et al., 2007). A modification of the SPME technique allows the sampling of the headspace of a sample (HS–SPME), rather than the direct immersion of the fibre into the sample matrix. HS–SPME provides a direct measurement of vapour phase chemical concentrations assumed to be equilibrated with solution at the time of sampling and enables calculation of the freely-dissolved HOC concentration through use of the Henry's law constant for the solute in question. Owing to the very high capacity of the SPME fibre relative to the vapour phase, it is generally assumed that the entire chemical mass associated with HS-SPME is rapidly scavenged onto the fibre negating need for measuring a separate SPME fibre/air partition coefficient. Using this approach, the freely dissolved water concentration can be assessed even in ‘dirty’ matrices, such as MWTP effluents and complex multi-phase solutions while maintaining clean analytical conditions (Vaes et al., 1996).

Cosolvent effects have been thoroughly investigated for solvent/solute effects (Munz et al., 1986; Dickhut et al., 1989; Resendes et al., 1992; Nzengung et al., 1996; Bouchard, 1998; Fernández-González et al., 2007; Smedes et al., 2009). The consensus of these studies is that an exponential increase in water solubility occurs for low and moderately soluble solutes with a linear increase in cosolvent volume fraction (v/v% denoted as f_c). Thus, increasing cosolvent f_c results in increased apparent solubility of HOCs. However, these effects are only considered significant above 10% (v/v), which is markedly higher than typical cosolvent volumes used in solubility and partitioning studies that use batch spiking experiments (Munz et al., 1986; Banerjee et al., 1988). Despite this consideration of a high cosolvent volume ratio needed to affect solubility, many researchers have used the generator column technique, which omits cosolvents completely (May et al., 1978a; May et al., 1978b; Friesen et al., 1985; Friesen et al., 1990; Hong et al., 1995; de Maagd et al., 1998). Solubility’s measured using the generator column techniques has often produced lower solubility estimates than those reported using spiked samples (de Maagd et al., 1998). Given these results appear to conflict with the 10% volume fraction hypothesis stated above, further examination of cosolvent effects at f_c additions similar to those employed in solubility experiments are warranted. With the addition of potential solvent/sorbent effects further affecting solute behaviour (Bouchard, 2003); the assessment of cosolvent effects is also important in determination of partitioning behaviour (K_{COC}) in studies that utilize spiking techniques.

A second consideration in spiked experimental designs is sorption of HOC to various vial surfaces as well as loses of solute from the system over time. The predominant surface in these batch-type experiments are glass walls but also include PTFE-coated septa and cap surfaces. If chemical is sorbed to glass walls, it may also be more easily hydrolyzed (Brown et al., 2005; Brown 2006). Silanization of glass has been used historically as a means to reduce binding of HOCs (Potter et al., 1994; Langenfeld et al., 1996; Doong et al., 2000; Brachet et al., 2005). Surface binding of chemical, and subsequent reduction in soluble chemical, is of great importance for batch-type samples that need extended equilibration times. This includes spiked MWTP samples, which are typically given a 24 h equilibration period meant to mimic actual retention times in the MWTP system. Chemical losses are not easy to quantify in batch type experiments, especially given that mass balances are not usually performed in these studies because only one phase (freely-dissolved concentrations) are measured and concentration of solute in the organic phase is estimated by difference. Given these difficulties in quantification, potential for sorption of solute to vial walls and/or losses of solute during equilibration, it is of utmost importance to characterize systematic errors related to the above artefacts using batch experiments and HS-SPME methodologies.

The goal of this research is to determine the effects of experimentally relevant f_c levels of the cosolvent MeOH on apparent solubility of chlorobenzenes under batch studies using HS-SPME methods commonly applied during measurement of K_{COC} values in wastewater samples. The study focuses on three chlorobenzenes (1,2,4,5-tetrachlorobenzene, pentachlorobenzene, hexachlorobenzene) which are historically significant HOCs and have well established solubility and partitioning behaviour within the literature. Further experiments include assessment of chemical stability over time in raw glass and silanized SPME headspace vials. The results of these experiments will be considered in cosolvent behaviour for future MWTP partitioning research.

2. Materials and Methods

2.1. Chemicals

1,2,4,5-tetrachlorobenzene (1,2,4,5-TeCB; 98% pure), pentachlorobenzene (PeCB; 98% pure), hexachlorobenzene (HCB; 99% pure), and sodium azide (NaN_3: 98% pure) were purchased from Sigma-Aldrich (Canada). A stock solution mixture of 30, 10, and 10 mg L^{-1} of TeCB, PeCB and HCB, respectively, was prepared in hexane and stored at 4 °C.

2.2.Vial preparation and silanization

SPME 20 mL crimp-top headspace vials (Varian #854181U) were used with teflon/silicon septa (Varian #27454U). Three silanization applications were considered including pre-silanized vials (VWR #69400-118), Sigmacote SL-2 (Sigma-Aldrich), and 5% dimethyldichlorosilane (DCMCS – Sigma-Aldrich). Both SL-2 and DCMCS were applied to vials as per product information available for SL-2 (Sigma-Aldrich) prior to use. All vials were soaked overnight in 5% RBS solution (Thermo Fisher Scientific), rinsed three times with deionised water and dried in a 250 °C oven for 4 h after use (for reuse if applicable).

2.3.Wastewater sampling

A 2 L grab sample was taken from Little River Pollution Control Plant (LRPCP) in Windsor, Ontario, Canada. The plant serves the eastern portion of the City of Windsor and the surrounding municipalities of Tecumseh, St. Clair Beach and Sandwich South, and has two parallel and similar activated sludge-type secondary wastewater treatment systems with a combined design capacity of 60 000 m^3 d^{-1}. The sample was transported to the laboratory within one hour of collection and treated with ca. 100 mg L^{-1} sodium azide to inhibit microbial degradation. The sample was allowed to settle (creating suspended solids – SS sample from the supernatant) and subsequently filtered through 0.45 µm precombusted glass fibre filters (Whatman Type WCN).

2.4. SPME apparatus

The experimental setup for the SPME sampling is shown in Fig. 1. All samples (12 mL) were placed into vials and spiked with 1.2 µL of the chlorobenzene mixture for a final MeOH concentration of 0.01% (v/v). Final chlorobenzene concentrations for all samples were well below reported solubility limits at 600, 200, and 200 pg mL^{-1} of TeCB, PeCB, and HCB, respectively. Small teflon coated flea bars were inserted, vials capped with teflon/silicon crimp tops, and stirred on a vortex for 2 min. A manual SPME fibre holder loaded with a 100 µm PDMS fibre (Sigma-Aldrich #57432U) (conditioned as per manufacturer recommendations) was inserted into a pre-punctured hole in the septa and exposed to the headspace of the vial for 30 min at 40 °C and 1600 RPM. The fibre was retracted and inserted into the GC injection port for 2 minutes for extraction (see below for GC-ECD conditions). SPME experiments were optimized for maximum extraction

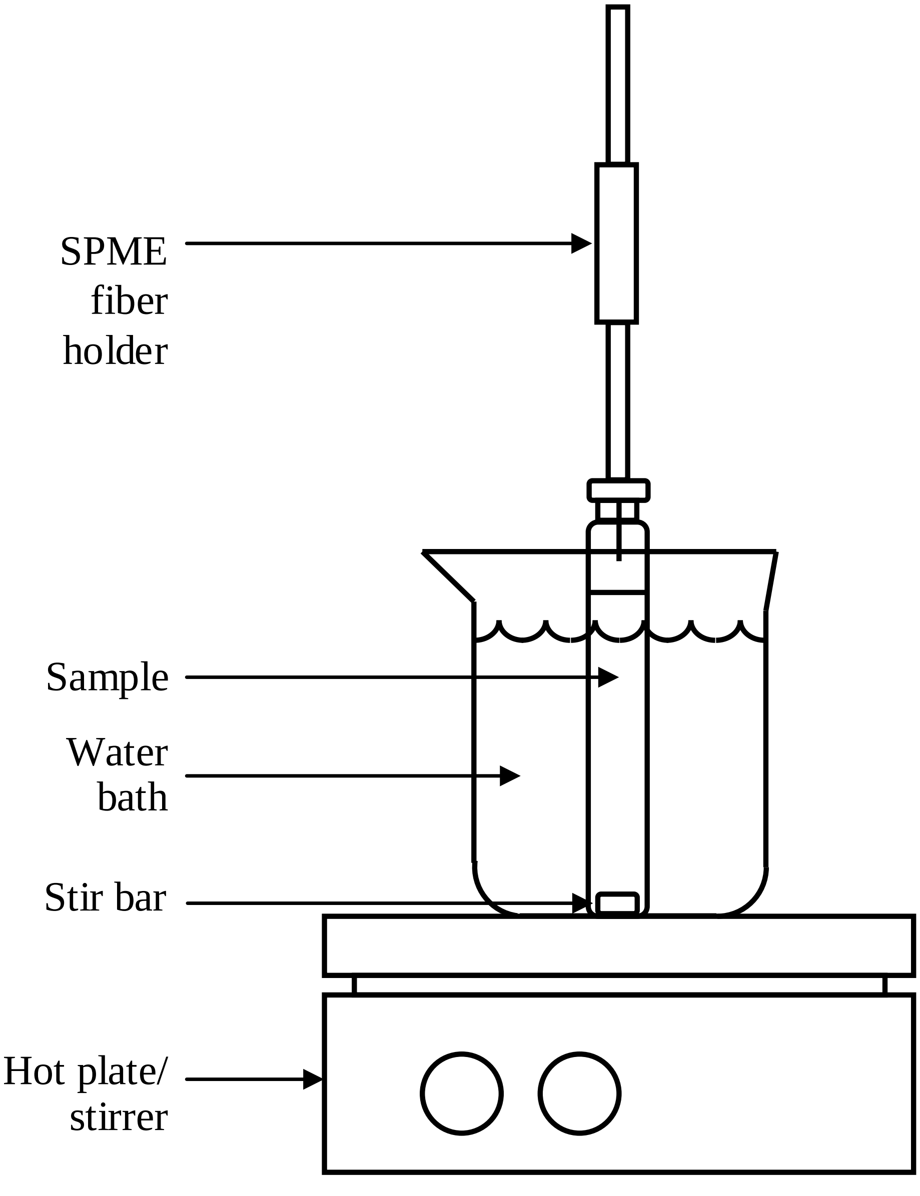

Fig.1: SPME experimental apparatus for head-space microextraction.

efficiency of chemical by varying time, temperature, and stirring prior to start of experiments.

2.5.Experiments

Experimental treatments included cosolvent, long-term, silanization, and effluents. Each experiment adhered to the SPME apparatus conditions considered previously.

2.6.Cosolvent effects

MeOH standard was spiked into MilliQ water. Subsequent volumes of MeOH were added to create additional treatments of 0.1, 1, 2, 5, and 10% methanol (v/v). At least four replicates per treatment were performed for each experiment. Cosolvent experiments were vortexed for complete mixing and immediately extracted.

2.7.Long-term equilibration studies

MeOH samples of 0.01 and 10% (v/v) (15 vials each) in MilliQ water were created as in the ‘Cosolvent’ section above. Samples were equilibrated at room temperature on a shaker at ca. 60 RPM. After 2, 24, 48, and 96 h three vials from each treatment were sacrificed and extracted using the SPME procedure. Control samples (21 vials), three replicates of 100% MeOH, were extracted at 2, 4, 6, 8, 24, 48, and 96 h to compare with 0.01 and 10% MeOH treatments.

2.8.Silanization

Silanization treatments included control (unsilanized vials), 24 h control, Sigmacote, 24 h Sigmacote, DCMCS, and 24 h DCMCS. MeOH silanization samples included three replicates for all treatments at 0.01% MeOH (v/v) in MilliQ water. 24 h samples were equilibrated at room temperature on a shaker at ca. 60 RPM before extraction.

2.9.Effluent

Effluent treatments included control (unsilanized vials), 0.45 µm filtered fraction, and SS fraction. MeOH standard was spiked into four replicates for each treatment and allowed to equilibrate at room temperature for 24 h on a shaker at ca. 60 RPM until extraction.

2.10. Analytical methods

Analysis of all samples was carried out on a Varian 3600 GC equipped with split/splitless injector, a 30 m X 0.32 mm fused silica DB-5 column with a 0.25 µm film thickness (J&W Scientific) and an ECD detector. The injector was maintained at 250 °C with a flow rate of 2 mL min^{-1} He. The fibre was desorbed for 2 min in a 253 µm liner. During desorption the column was held at 140 °C. Subsequently, the column was raised to 192 °C at 6.5 °C min^{-1} ramp. Makeup flow rate was 29 mL min^{-1} N_2 and detector temperature at 250 °C. The limit of detection (LOD) is defined as the minimum amount of analyte which produces a peak with a signal-to-noise ratio equal to 3. A PeCB standard was injected prior to and post all experimental runs as quality control and expected to fall within a standard deviation of standard curve values.

3. Results and Discussion

3.1.Cosolvent limits

Results of MeOH cosolvent experiments are presented in Fig. 2. All three chemicals exhibit a log – linear decreasing relationship between solvent fraction and extracted mass vapour phase solute. This result is similar to reduced headspace measurements for chlorobenzenes by Resendes et al., (1992), where increasing octanol volume ratio decreased measured headspace concentrations. However, the octanol relationship was not log – linear since octanol is only partially miscible in water, while MeOH in the current study is completely miscible and should exhibit log – linear behaviour (Pinal et al., 1990). Given that the HS-SPME method allows the calculation of freely-dissolved chemical after extraction of the headspace chemical (Vaes et al., 1996), the decrease in mass extracted must be considered as increased mass in liquid attributed to the increase in apparent solubility caused by the MeOH cosolvent. In this case, the increase in apparent solubility has a similar effect as a sorbent to the HOCs according to solvophobic theory since there is an increase in overall liquid-phase capacity (Nkedi-Kizza et al., 1985; Fu et al., 1986; Rao et al., 1989). All 3 chlorobenzenes had statistically similar slopes ($p>0.05$; ANCOVA) (Fig. 2), which indicates the relationship between cosolvent and chlorobenzenes is constant. This is in contrast to Resendes et al. (1992) where miscible-region slopes were variable. Given the very similar molecular volumes of the 3 chlorobenzenes, differences in the cosolvent and solvent molecular interactions involving ‘cavity’ formation for chemical insertion would be minimal; therefore, similar slopes would be expected for these 3 chemicals with MeOH cosolvent.

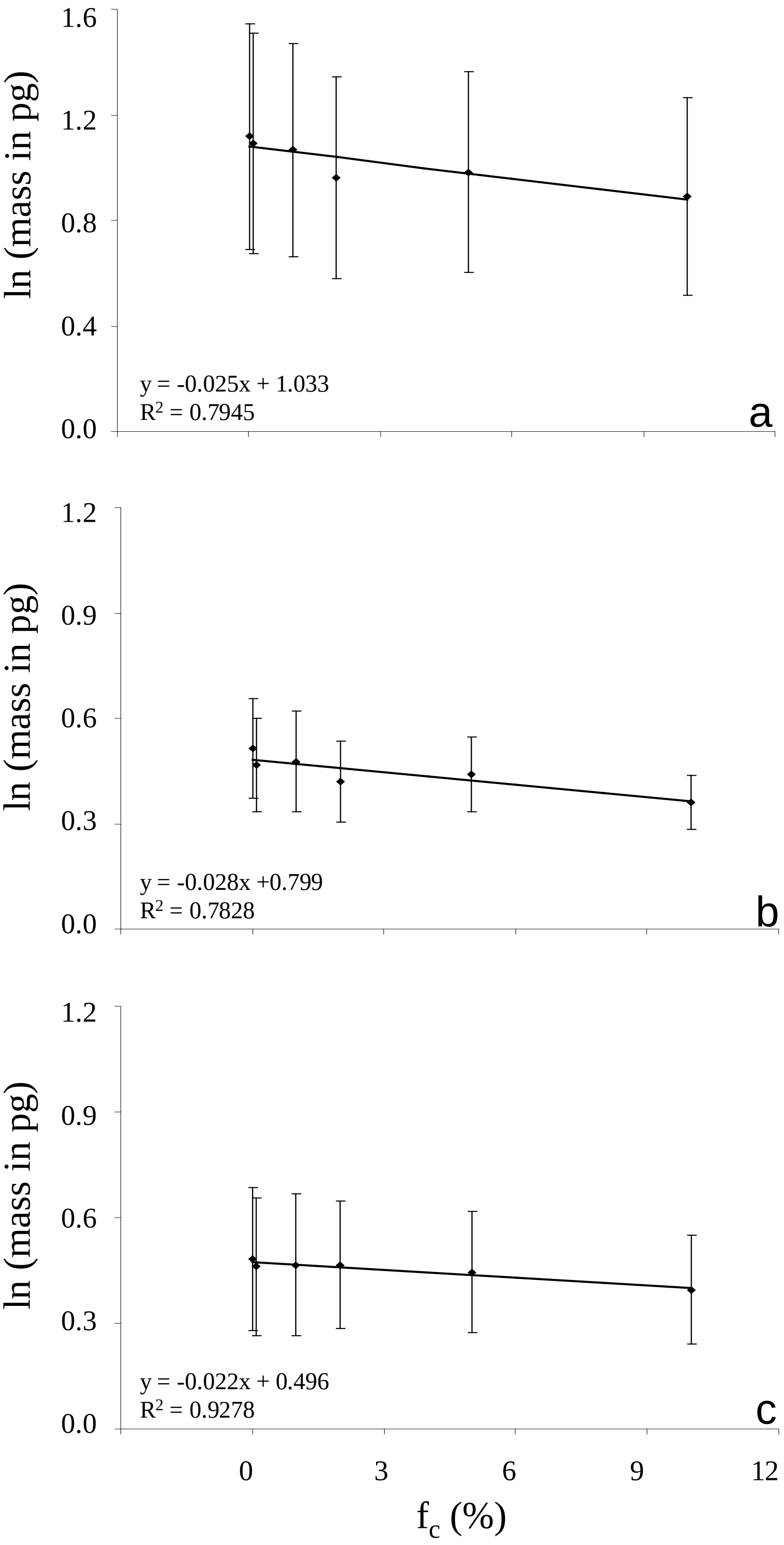

Fig 2: Mass of each chemical extracted via the SPME fiber in comparison to various volume fractions of MeOH. (a)TeCB; (b) PeCB; (c) HCB.

Cosolvents have been shown to increase the solubility of HOCs above solubilities in pure water (Dickhut et al., 1989; Dickhut et al., 1991; Yalkowsky et al., 1981). MeOH in the current study increased the apparent solubility of chemical and reduced the vapour phase concentration in the headspace vials in a linear manner, but such effects only became noticeable within error at higher MeOH volume fractions. At MeOH spiking volumes of 0.01, 0.1, and 1%, there were no significant differences ($p>0.05$; ANOVA for each chlorobenzene) in vapour phase chemical mass extracted from the control (0.01% MeOH). However, the remaining concentrations 2, 5, and 10% exhibited statistically significant ($p<0.05$; ANOVA) lower vapour phase masses from the control (0.01% MeOH) volume fraction addition. Given these results, any MeOH concentration 1% (v/v) and below should be considered reasonable for spiking of chlorobenzenes. However, these experiments have not considered potential solvent/sorbent behaviour which has been shown to affect partitioning (Bouchard, 2003). Therefore, spiking with the lowest possible MeOH concentration (0.01%) should be considered for partitioning experiments as an extra precautionary measure to avoid cosolvent artefacts.

Generator column usage has been shown to be beneficial in accurate determination of aqueous solubilities (May et al., 1978a; May et al., 1978b; Friesen et al., 1985; Friesen et al., 1990; Hong et al., 1995; de Maagd et al., 1998). Unfortunately, due to low solubilities of HOCs in water coupled with very high capacity of organic phases added to samples in such experiments, cosolvents must be used in order to introduce high enough chemical mass in batch systems to achieve measurable aqueous concentrations in partitioning experiments. Most batch experiments performed to measure chemical partitioning to COC utilize cosolvent spiking apply cosolvent volumes that typically range from 0.01 – 1.0 % for literature values (Kopinke et al., 2001; Paschke et al., 2003;

ter Laak et al., 2005; Endo et al., 2008; Mei et al., 2009; Bohm et al., 2010), although few studies mention the importance of the cosolvent concentration or that it was investigated prior to conducting sorption and partitioning studies (Backhus et al., 1990; Backhus et al., 2003). This study supports the use of MeOH cosolvent at volumes applied in the above cases but such relationships may not hold for all solutes. Experimental validation to test for cosolvent artefacts should be conducted and reported on a more routine basis in conjunction with batch experiment results which use cosolvent spiking as a means of adding the solute to the batch systems.

3.2.Long-term and silanized batch vials

Long-term MeOH experiments (24 h) were considered since MWTP samples must be given an appropriate time interval for partitioning to approach or reach equilibrium after spiking in laboratory. This duration was considered for MWTP samples since it is reasonably close to actual hydraulic and solids retention times within municipal wastewater treatment plants. Actual equilibrium of chemical onto suspended solids may not be attained during this time period; however, equilibrium with COC may occur given literature suggestions for equilibrium between water/DOM components range from minutes to weeks (Kopinke et al., 2001; Ter Laak et al., 2005; Endo et al., 2008; Mei et al., 2009; Bohm et al., 2010). Time periods exceeding 24 h equilibration are more suitable for solids (soils and sediments) since the HOC/particle contact time usually occurs over longer durations and the heterogeneity of particle matrices makes sorption kinetics very slow (Karickhoff et al., 1985).

Results of longer-term MeOH chemical equilibration trials are shown in Fig. 3, with mass losses considered in Table 1. Control samples (100% MeOH) were stable for

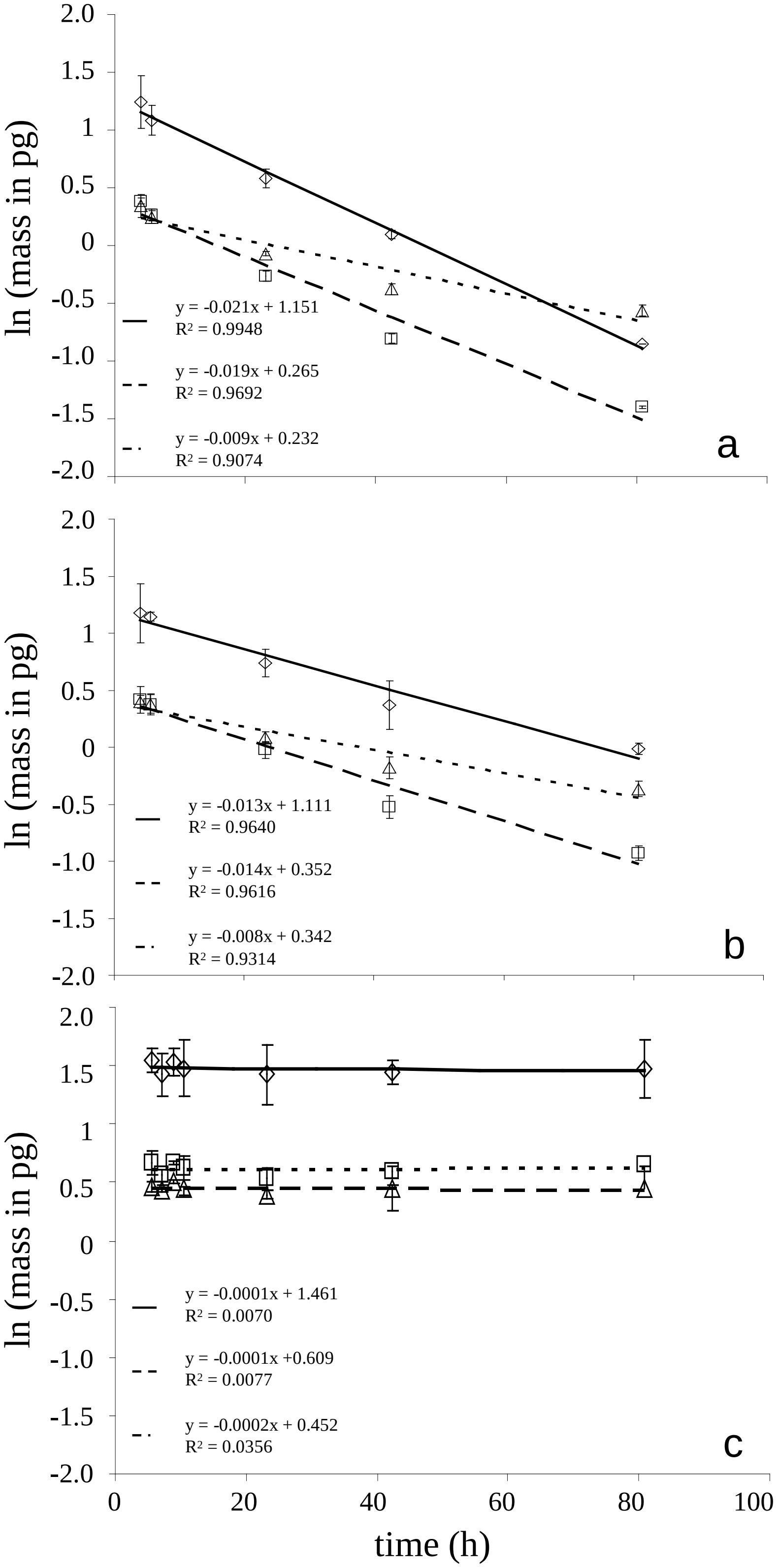

Fig. 3: Unexplained loss of chemical: (a) 0.01% MeOH; (b) 10% MeOH; (c) 100% MeOH. Symbols represent: TeCB – diamonds; PeCB – squares; HCB – triangles.

all chemicals over the duration of the study (Fig. 3c). Both 0.01 and 10 % MeOH treatments demonstrated major chemical reductions in extracted headspace chemical mass over the four day time period, with faster declines observed in the 0.01% treatments. Reductions in chemical mass in headspace were exponential, with rates being similar for TeCB and PeCB, while the loss rate of HCB was slower (Fig. 3a,b). After 96 h, only 12.3, 16.8, and 40.4% of TeCB, PeCB, and HCB, respectively, were extracted in headspace compared to the 2 h time point in the 0.01% MeOH treatment (Table 1). After the same time period, 30.4, 26.1, and 46.4% of TeCB, PeCB, and HCB, respectively, were extracted relative to the 2 h time point in the 10% MeOH treatment (Table 1). Similar losses have been reported by He et al. (2000), however, the sources of these losses were not considered.

Given that in each case the chemical was introduced into the aqueous phase first, as opposed to introducing directly into headspace, the observed trends in vapour phase chemical concentrations are not consistent with equilibration kinetics and re-distribution due to partitioning. Loss sources within the vial may include degradation and volatilization; additionally, HOCs may also partition to vial walls, stir bars and septa. Degradation was considered unlikely to be a major loss process due to the persistence of the chlorobenzenes in general, being long-term environmental pollutants with long half-lives (Table 1). Volatilization may occur via loss due to seal integrity and diffusion through the septa. Seal integrity has been shown to be a potential area of concern, especially with elevated temperatures (Schumacher et al., 2000; Costanza et al., 2008). Diffusion through polymer membranes has been reported (Baker, 2004; Brown, 2006) and can be significant for volatile compounds at elevated temperatures. Sorption has been extensively reported, especially to vial walls (Potter et al., 1994; Langenfeld et al., 1996; Ackerman et al., 2000; Costanza et al., 2008) and would be a major area for further investigation. Degradation of persistent chlorobenzenes, especially over short term experiments, is unlikely. Potential degradation mechanisms include hydrolysis, photolysis, and biodegradation. Hydrolysis and biodegradation half-life values for chlorobenzenes can be found in the literature (Table 1); however, photolysis of chlorobenzenes has not been reported. Biodegradation is not considered in the current study since MilliQ water was used; additionally, sodium azide was used in MWTP samples which would inhibit biodegradation. Vials were spiked and covered with foil during equilibration to inhibit potential photolysis. The resultant foil-covered vials were found to exhibit similar losses to uncovered vials, therefore photolysis was not considered a major loss process. Volatilization could be a potential loss process. Another set of vials were spiked and sealed with a polyfilm layer placed into a 4 °C refrigerator overnight. Sampling was still considered at 40 °C; however, the vial was kept covered with polyfilm for the equilibration period. These experiments were unsuccessful in reducing apparent losses related to reduction in solute headspace concentrations with time. Sorption to vial walls, septa and stir bars has been previously studied. To determine sorption, vials were processed for experiments as normal (24 h equilibration). After processing, headspace samples were taken using a large-bore syringe and found to have negligible chemical content after SPME extraction. Vials were subsequently opened, 10 mL of hexane was added, resealed and shaken for 2 h to extract sorbed and dissolved chemical. Approximately 50% of the lost chemical was extracted using this procedure. However, samples left for longer durations declined to negligible concentrations. Due to the persistence of the chlorobenzenes, a major potential chemical sink or escape pathway

Table 1: Percentage of total mass available for SPME extraction after various equilibration times versus non-equilibrated samples. Potential loss process half-lives for each chemical taken from Howard et al. (1991). Sorption partitioning coefficients to stir bars, glass walls and septa are unavailable.

	treatment						
	0.01%		10%		half-life, $t_{1/2}$		
chemical	time (h)	mass (%)	time (h)	mass (%)	hydrolysis (y)	photolysis	biodegradation (h)
TeCB	0	100	0	100	900	nd	672–4320
	2	85.4	2	96.8			
	24	51.6	24	64.6			
	48	31.8	48	44.8			
	96	12.3	96	30.4			
PeCB	0	100	0	100	900	nd	4656–8280
	2	88.6	2	96.3			
	24	52.3	24	64.6			
	48	30.4	48	39.1			
	96	16.8	96	26.1			
HCB	0	100	0	100	nd	nd	23256–50136
	2	90.7	2	97.7			
	24	66.0	24	73.2			
	48	48.6	48	56.1			
	96	40.4	96	46.4			

may be the vial septa, which would not be easily extracted due to chemical permeation through the septa material.

The potential for sorption to glass walls has been well studied. With sorption to walls, chemical may potentially degrade faster due to hydrolysis (Brown et al., 2005; Brown 2006). Silanization of glass has been used extensively in an attempt to decrease binding of HOCs (Potter et al., 1994; Langenfeld et al., 1996; Doong et al., 2000; Brachet et al., 2005). To determine effects of silanization, three silanization solutions were tested (see Methods). Results of silanization headspace masses are presented in Fig. 4 (results of pre-silanized vials omitted for clarity due to similar results to Sigmacote). Both silanization methods resulted in a statistically significant increase in adsorption to vial walls for both instantaneous and 24 h samples. Sigmacote sorption was highest for HCB and lowest for TeCB for both instantaneous and 24 h samples, with reductions in headspace masses extracted ranging from 18 – 67% of control vial experiments (Fig. 4). DCMCS sorption was extremely high for all chemicals, ranging from 86.3 – 94.5% of control vial experiments. Reasons for conflicting results of the current study with literature values are unknown and need further examination.

3.3.Effluent samples

Despite the inability to properly equilibrate MWTP samples for 24 h, samples were allowed to equilibrate for 2 min to determine if partitioning processes are occurring at relevant quantities for further studies. Results indicate that rapid sorption to MWTP COC and suspended solids occurred in both sample types after this short interval, with major decreases in extracted mass in headspace of COC and SS containing vials relative to controls (Fig. 5). SS samples sorption was greater than that of 0.45 µm samples, with

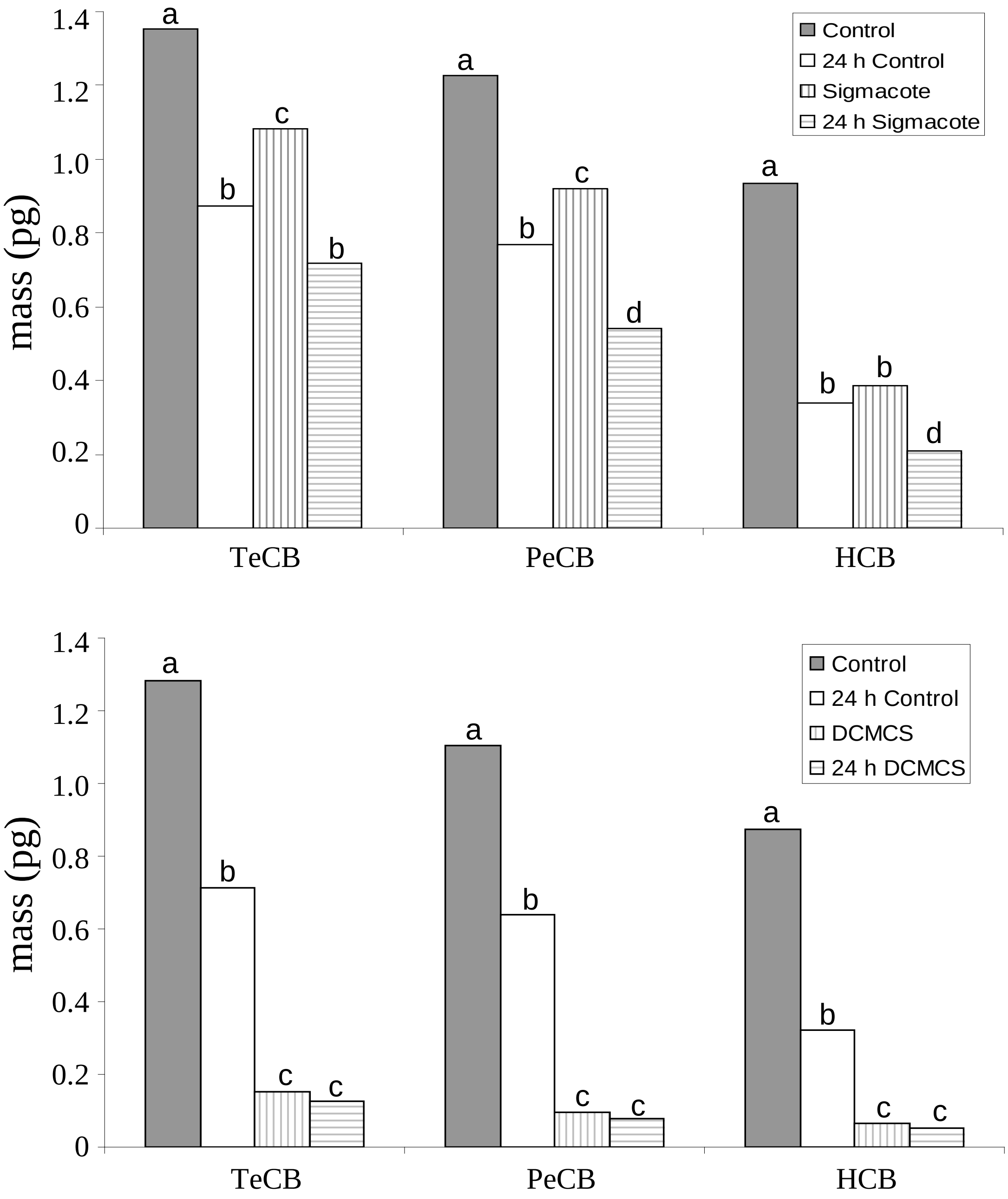

Fig. 4: Mass of chemical extracted via SPME extraction. Samples include two silanizing agents, Sigmacote and DCMCS. Letters above each individual bar designate statistical results for each data series; like symbols indicate results being similar (p>0.05; ANOVA).

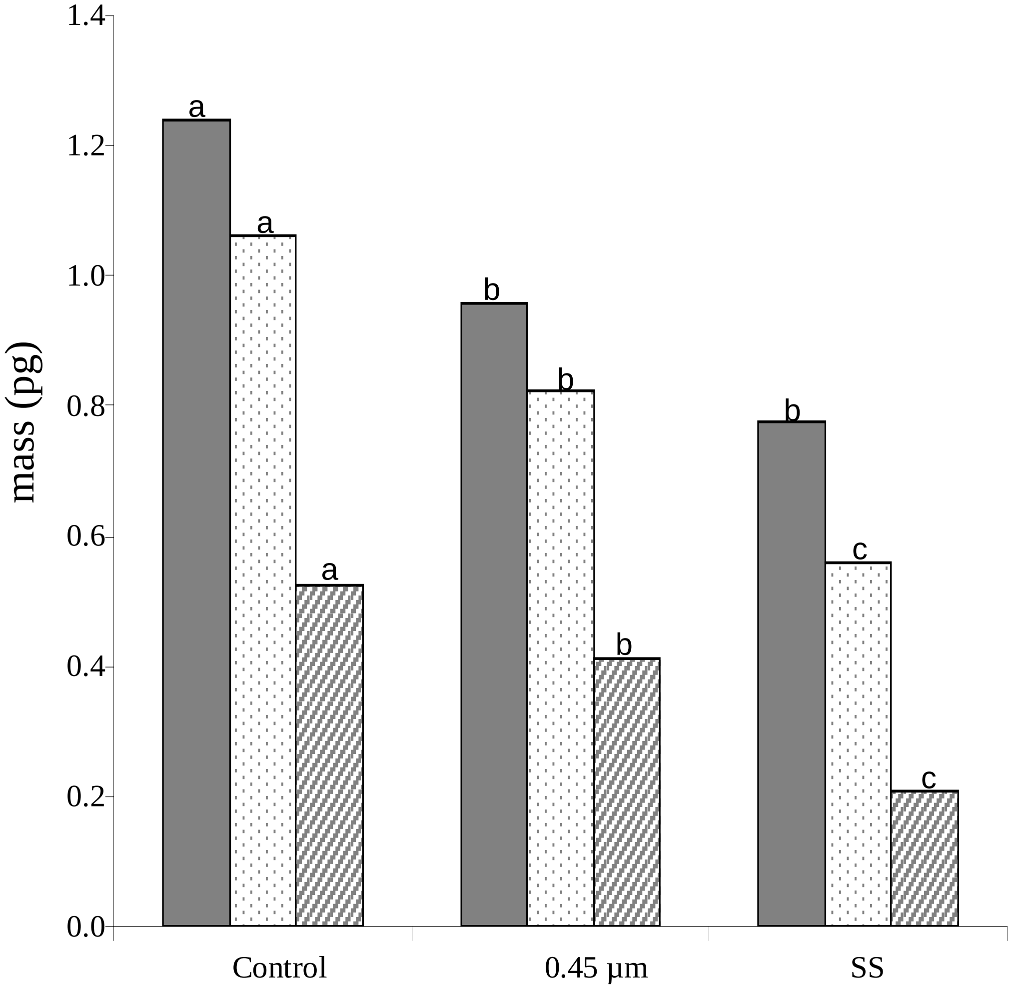

Fig. 5: Mass of chemical extracted via SPME for control, 0.45 µm, and suspended solids samples. Shading represents: TeCB – grey; PeCB – dots; HCB – angle. Letters above each individual bar designate statistical results for each data series; like symbols indicate results being similar ($p>0.05$; ANOVA).

statistically greater sorption for PeCB and HCB. Although not statistically significant for TeCB, sorption to SS samples was markedly higher (Fig. 5). Results overall indicate that sorption of the chlorobenzenes over short equilibration times is significant but further study to deduce equilibration times is needed to establish partition coefficients. Unfortunately, significant losses observed during equilibration in long term incubation trials can strongly confound K_{COC} estimates, especially if a system mass balance is not completed at the end of the trial. Given these concerns, HS-SPME is not considered a valid method for use in partitioning behaviour experiments in which extensive equilibration periods are needed.

4. Conclusions

Determination of partitioning behaviour of HOCs in MWTPs and other environmental matrices is important in analyzing chemical fate. The ability to measure freely-dissolved fractions of 'dirty' matrices such as MWTP samples is invaluable to research on partitioning behaviour. Many studies have relied on spiking of HOCs into matrices to discern partitioning behaviour. Due to low solubilities of these HOCs, generator column produced freely-dissolved samples do not introduce sufficient solute mass to a system and therefore solvents must be used for spiking. The role of these cosolvents has been investigated at higher volume fractions. However, cosolvent effects have historically been considered as negligible at cosolvent spiking concentrations below 1%. This study validated use of MeOH volumes of 1% and lower, but significant cosolvent effects were noted at 2% and greater MeOH concentrations. Given that cosolvent effects are often solute specific and may also interact with COC, it is suggested that investigation and reporting of cosolvent effects be incorporated as part of the experimental design in standard batch study systems. SPME is a valuable method in measuring freely-dissolved concentrations and has increased markedly as a tool in experimental sorption studies. Despite its benefits, chemical loss processes in small headspace vials used for this method were significant and could not be elucidated following several experimental manipulations. These chemical losses through time would have a confounding effect on the interpretation of sorption kinetics especially when chemical measurements are only made in the dissolved phase while the COC or SS associated chemical is extrapolated by difference. Validation of the system specific chemical sorption and conduct of mass balance recovery experiments are therefore required when performing batch type experiments with headspace vials as examined in the present research.

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CHAPTER 3

Henry's law constants and structure-property relationships of chlorobenzenes: Evaluation of the role of sorption to glass surfaces using a gas sparging system.

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1. Introduction

Henry's law constant (HLC) is a parameter used to describe the mass transfer of chemical between water and air. HLC is an important factor used in environmental risk assessment and fate and transport models (ten Hulscher et al., 2006). Additionally, HLC may also be used in fugacity models in conjunction with standard partition coefficients to calculate the fugacity capacity, reflecting a measure of the media/air partition coefficient (Mackay and Paterson, 1981a). Despite the need for an accurate determination of HLC, the quality and uncertainty of measured physicochemical data (including HLC) has recently been questioned (Goss et al., 2004; Brachet et al., 2005; Jantunen and Bidleman, 2006; ten Hulscher et al., 2006; Qian et al., 2011). Although, accurate determination of these data are demanding, accurate HLC values are needed to avoid misinterpretation and invalid conclusions based upon flawed parameters (Goss et al., 2004).

HLC may be determined by many experimental and estimation methods. In the absence of measured data, vapour pressure (P) and aqueous solubility (S) may be used to estimate HLC (HLC = P/S); this method is simply an estimate and may lead to incorrect values (ten Hulscher et al., 1992). Measuring HLC directly by experimental methods is considered the most reliable and several methods have been assessed and discussed previously (Mackay and Paterson, 1981a; Fendinger and Glotfelty, 1989). In the current study, the gas sparging method is used. Gas sparging has been used extensively for calculation of HLC for sparingly soluble and semivolatile compounds (Oliver 1985; Yin and Hassett, 1986; Warner, 1987; Dunnivant et al., 1988; ten Hulscher, 1992; Drouillard et al., 1998; Jantunen and Bidleman, 2006; ten Hulscher, 2006). Determination of HLCs for hydrophobic organic compounds (HOCs), such as chlorobenzenes, may be difficult due to low solubilities and low HLCs (ten Hulscher et al., 2006). Additionally, experimental artefacts related to sorption of chemical to sparger glass walls (or any glass surfaces) is a known issue for HOCs and may lead to faster degradation (Brachet et al., 2005; Brown et al., 2005; Brown 2006; ten Hulscher et al., 2006; Qian et al., 2011). Given the dynamic experimental system established in the sparger, some of these artefacts may be minimized in gas sparging systems as compared to batch systems. However, it is important to consider these potential sources of error both during experimentation and in subsequent calculations to establish accurate HLCs.

An environmentally relevant suite of HOCs are the chlorobenzenes, some of which are listed as priority pollutants by the US Environmental Protection Agency (USEPA). Chlorobenzenes are a suite of varying physicochemical properties (Table 1). Three compounds (1,2,4,5-tetrachlorobenzene – TeCB, pentachlorobenzene – PeCB, hexachlorobenzene – HCB) were chosen for the current study. Each of these chlorobenzenes, especially HCB, have numerous literature HLCs available (see Table 2). The goal of the current study is to establish HLCs for the three chlorobenzenes using the gas sparging technique considering the potential of adsorption to glass surfaces. Given the wide range of literature HLCs, determination of accurate HLCs are valuable in future use of gas sparging in the determination of partitioning behaviour with organic matter such as samples derived from MWTP or natural sources are to be considered in subsequent studies. A secondary goal of this study is the determination of potential HLC correlation to various structural property relationships.

Table 1: Physicochemical properties of the chemicals at 25 °C

						log K_{ow}	
chemical	**MW**	**CAS#**	**V_p(Pa)**[a]	**solub.(g m^{-3})**[a]	**S_M**[b]	**selected**[a]	**range**[c]
TeCB	215.9	95-94-3	9.86	1.27	175.2	4.5	4.46 – 5.05
PeCB	250.3	608-93-5	0.88	0.65	192.3	5	4.88 – 5.79
HCB	284.8	118-74-1	0.245	0.005	209.4	5.5	4.13 – 6.53

[a] Suntio et al., 1988; [b] Surface area (S_M) in angstroms: Sabljic, A. 1987; [c] References found within Suntio et al. 1988

2. Theory

Gas spargers are spiked with HOCs and allowed to reach equilibrium with sparger surfaces overnight. Nitrogen gas is bubbled through the column height, allowing equilibrium between gas and water to occur. HLC can be determined via (Drouillard et al., 1998):

$$HLC = k_v \frac{VRT}{F} \tag{1}$$

where V is the sparged water volume (L), R is the gas constant, T is temperature (K), F is the gas flow rate (L h^{-1}), and k_v is the first-order volatilization rate constant (h-1). The volatilization rate constant (k_v) can be found via (Dunnivant et al., 1988):

$$\ln(m_{w(o)} - m_{air}) = -k_v t \tag{2}$$

where $m_{w(o)}$ is the initial mass in the sparger and m_{air} is the mass captured at the sparger outlet. A plot of $\ln(m_{w(o)} - m_{air})$ versus t allows the k_v term to be found via the slope.

Two assumptions must be valid for these equations to hold: (1) the sparged gas must reach equilibrium with the water; (2) k_v must be constant (linear) over the sparging duration (HLC is constant at a specified temperature).

3. Materials and Methods

3.1.Chemicals and reagents

1,2,4,5-tetrachlorobenzene (98% pure), pentachlorobenzene (98% pure), hexachlorobenzene (99% pure), 1,3,5-tribromobenzene (TBB; 98% pure) and Amberlite XAD2 (20-60 mesh) were purchased from Sigma-Aldrich (Canada). Stock solutions of 10 mg L^{-1} TBB (internal standard) and a mixture TeCB, PeCB and HCB (30, 10, and 10 mg L^{-1}, respectively) were prepared in hexane and methanol, respectively, and stored at 4 °C.

3.2.XAD2 resin trap preparation and extraction

XAD2 resins were cleaned prior to use using a flow-through column and distilled water, methanol, and hexane (ca. 20 times bed volume each at 1 mL min^{-1}) successively. XAD2 resins were dried using a nitrogen stream following cleaning. Resin traps consisted of pasteur pipettes (7 mm ID) packed with ca. 3 cm of dried XAD2 and the adsorbent was contained using glass wool plugs at each end (see inset Fig. 1). Teflon tubing was heated and pressure fit onto the pipette on each end. A luer fitting was added to the downstream end of the pipette for connection of an electronic flow gauge during experimentation and a vacuum manifold for extractions. XAD2 resin traps were stored at 4°C and reused for each experiment once verified clean via hexane extraction and gas-chromatography (see below). XAD2 resin traps were spiked with TBB prior to experimental use as an internal standard to verify extraction efficiency. Following sampling, each sampler was extracted using three 10 mL aliquots of hexane at ca. 0.5-1 mL min^{-1}. The first two aliquots were brought to 20 mL using hexane and placed into 30 mL storage vials without further processing and stored at 4°C prior to analysis by GC-ECD. The third aliquot was used only for verification of full extraction and XAD2 resin cleaning via GC-ECD.

3.3.Multi-sparger system

A multi-sparger system (max. 6 simultaneous) was used for all experiments (Fig. 1). The apparatus consists of a high-purity nitrogen gas stream pre-wetted via a pre-sparger delivered to a 6-port manifold (individually valved). Each port delivers ca. 50 mL min^{-1} nitrogen to a 1 L sparger (measured using an electronic flow controller). Spargers were kept at 25 °C (± 0.5 °C) via a circulating water bath.

Duplicate or triplicate 1 L samples of MilliQ water were spiked with 50 µL of the chlorobenzene mixture (30, 10, and 10 ng µL^{-1} of TeCB, PeCB, and HCB, respectively), mixed via hand-shaking and allowed to equilibrate ca. 18–24 h in the water bath prior to commencing experiments. Prior to initializing experiments, XAD2 resin traps were spiked with the TBB internal standard and placed at the outlet of each sparger. Flow rates were corrected to 45 – 55 mL min^{-1} after changing each adsorbent (1 h intervals to 12 h, 4 h intervals to 24 h, and 12 h intervals to 48 h) to allow for variability in flow characteristics given the shared manifold. The overall sampling duration was reduced after initial experiments indicated a non-linear volatilization rate (see Results and Discussion) to 12 h with increased sampling accordingly (0.5 h intervals to 6 h, 1 h intervals to 12 h). XAD2 resin traps were removed and replaced at the above sampling

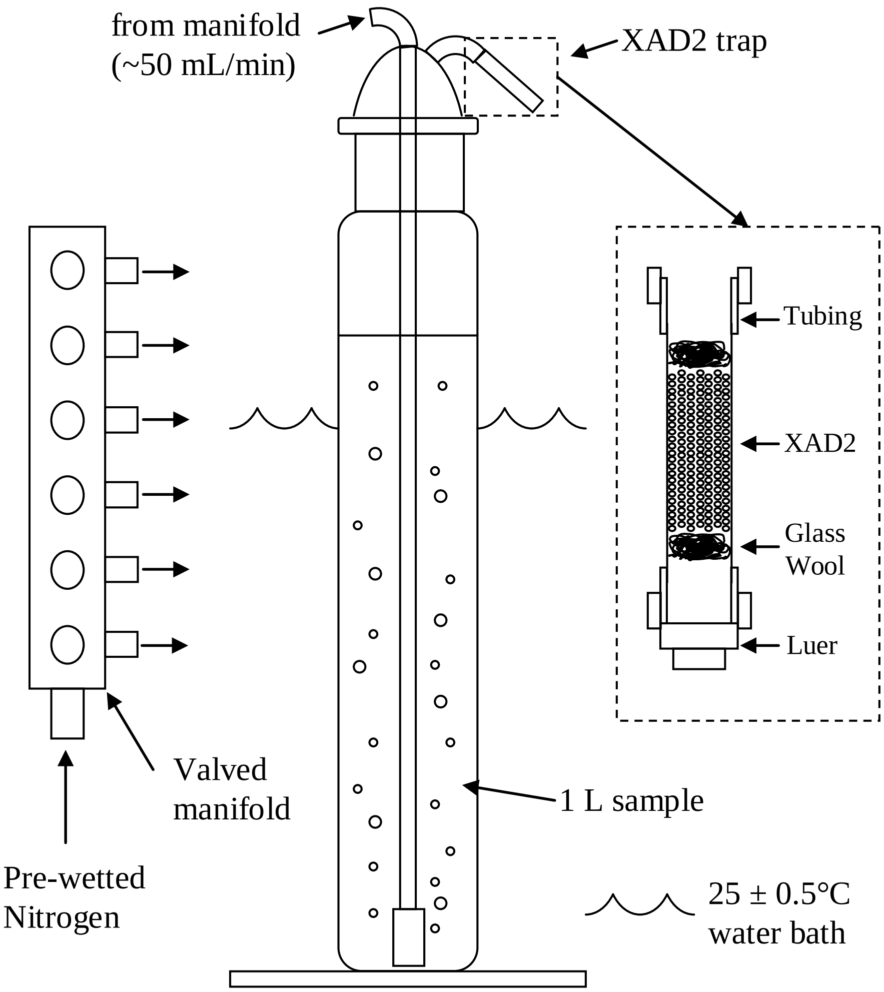

Fig. 1: Purging and XAD2 apparatus. Valved manifold attaches to up to 6 individual spargers that allow simultaneous replicates of control and treatment solutions.

intervals. Following removal, the resin trap was capped using polyfilm and placed in sealed bags at 4 °C until extracted as described above.

3.4.Analytical methods

Analysis of all samples was carried out on a Varian 3600 GC equipped with split/splitless injector, a 30 m X 0.32 mm fused silica DB-5 column with a 0.25 µm film thickness (J&W Scientific) and an ECD detector. The injector was maintained at 250 °C with a flow rate of 2 mL min^{-1} He. A 1 µL injection was made into a 253 µm liner and the column was held at 140 °C for 2 min. Subsequently, the column was raised to 192 °C at 6.5 °C min^{-1} ramp. The makeup flow rate was 29 mL min^{-1} N_2 and detector temperature at 250 °C. The limit of detection (LOD) is defined as the minimum amount of analyte which produces a peak with a signal-to-nose ratio equal to 3. A PeCB standard was injected prior to and post all experimental runs as quality control and expected to fall within a standard deviation of standard curve values. TBB standard recovery was 100 ± 6% over all sparger experiments.

4. Results and Discussion

4.1.Theory validation

The first assumption of the gas sparging technique is the sparging gas must reach equilibrium with the water phase. The column height equilibration assumption has been extensively studied (Mackay et al., 1979; Matter-Mueller et al., 1981; Yin and Hassett, 1986; Dunnivant et al., 1988; ten Hulscher et al., 1992; Drouillard et al., 1998). For the current chlorobenzenes, a 40 cm column was determined to be adequate for equilibrium (ten Hulscher et al., 1992); therefore, the current 60 cm water column height is considered acceptable for equilibrium and compares well with a recent 62 cm water column used by Jantunen and Bidleman (2006).

The second assumption of a constant k_v was investigated via plotting of eq. 2 and examining for breakpoints in the slope over time (Fig. 2). As is clearly apparent by Fig. 2, the volatilization rate exhibits three distinct regions, invalidating the assumption of a constant k_v during the sparging duration. Analysis of covariance (ANCOVA) was used to determine if the slopes differed between the three regions. This analysis was possible because of the robustness of the experimental sampling procedure including numerous replications (15 total spargers) and extensive data points available to discern key slope changes. The initial and transition zone regression line slopes did not differ statistically ($p>0.05$; ANCOVA). However, the third zone slope was statistically different than both the initial slope and transition slopes ($p<0.05$; ANCOVA). This statistical difference occurred for each chemical over each sparging experiment (typical experiment shown in Figs. 2 and 3). Therefore, given k_v is statistically different in the third slope region, use of the entire sparging data set would lead to a biased low HLC determination. Further, using the initial k_v to determine m_{air} using eq. 2, the expected cumulative mass was calculated over time and plotted along side of the realized cumulative mass versus time curve (Fig 3a-c). The actual mass purged begins to deviate from the expected curve at ca. 6 h and results in substantially less mass sparged material than theoretically expected based on the measured initial volatilization rate.

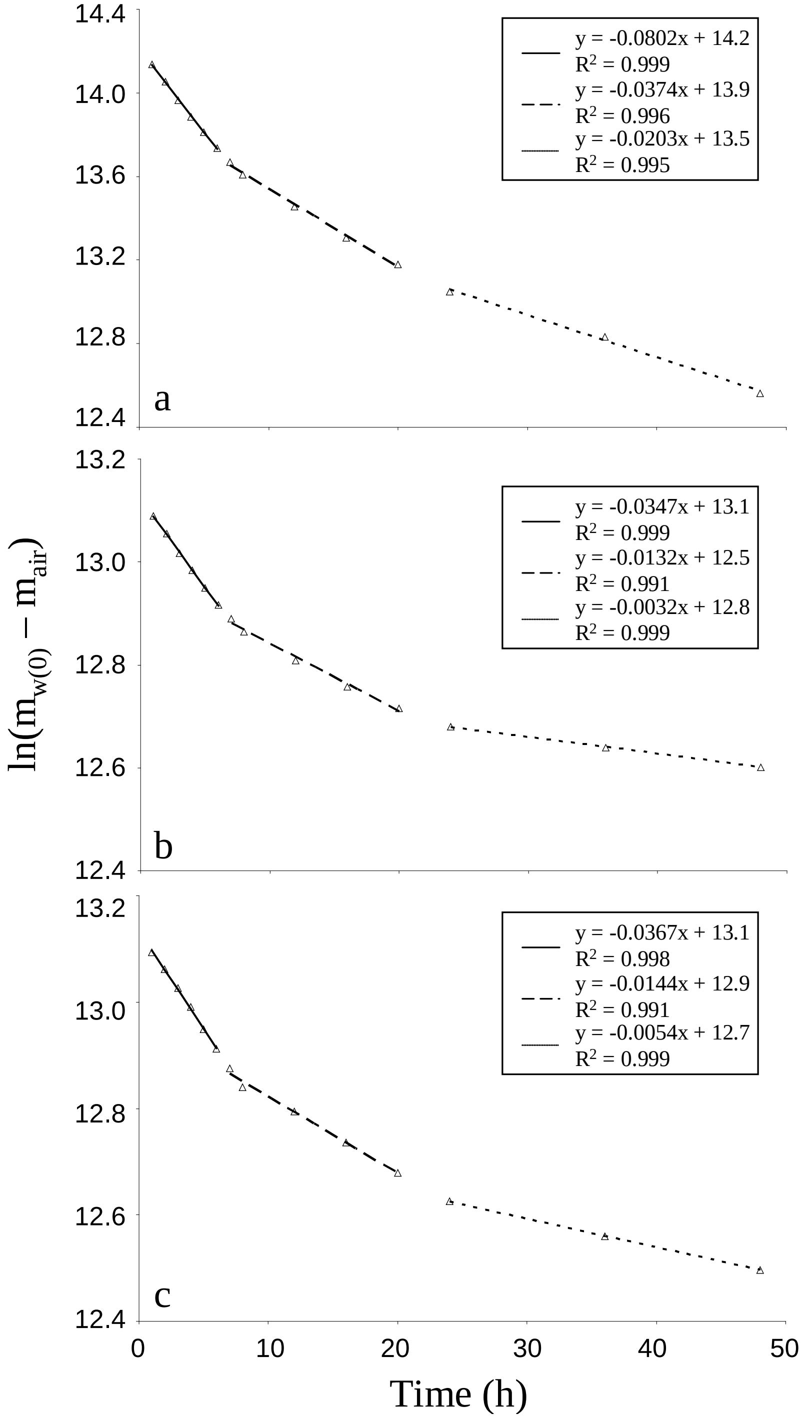

Fig. 2: Least squares linear regression of the natural logarithm of initial (spiked) minus measured cumulative mass (trapped) over time. Slope of initial regression line (see text for further detail) is the first-order volatilization rate constant (k_v). (a) TeCB; (b) PeCB; (c) HCB.

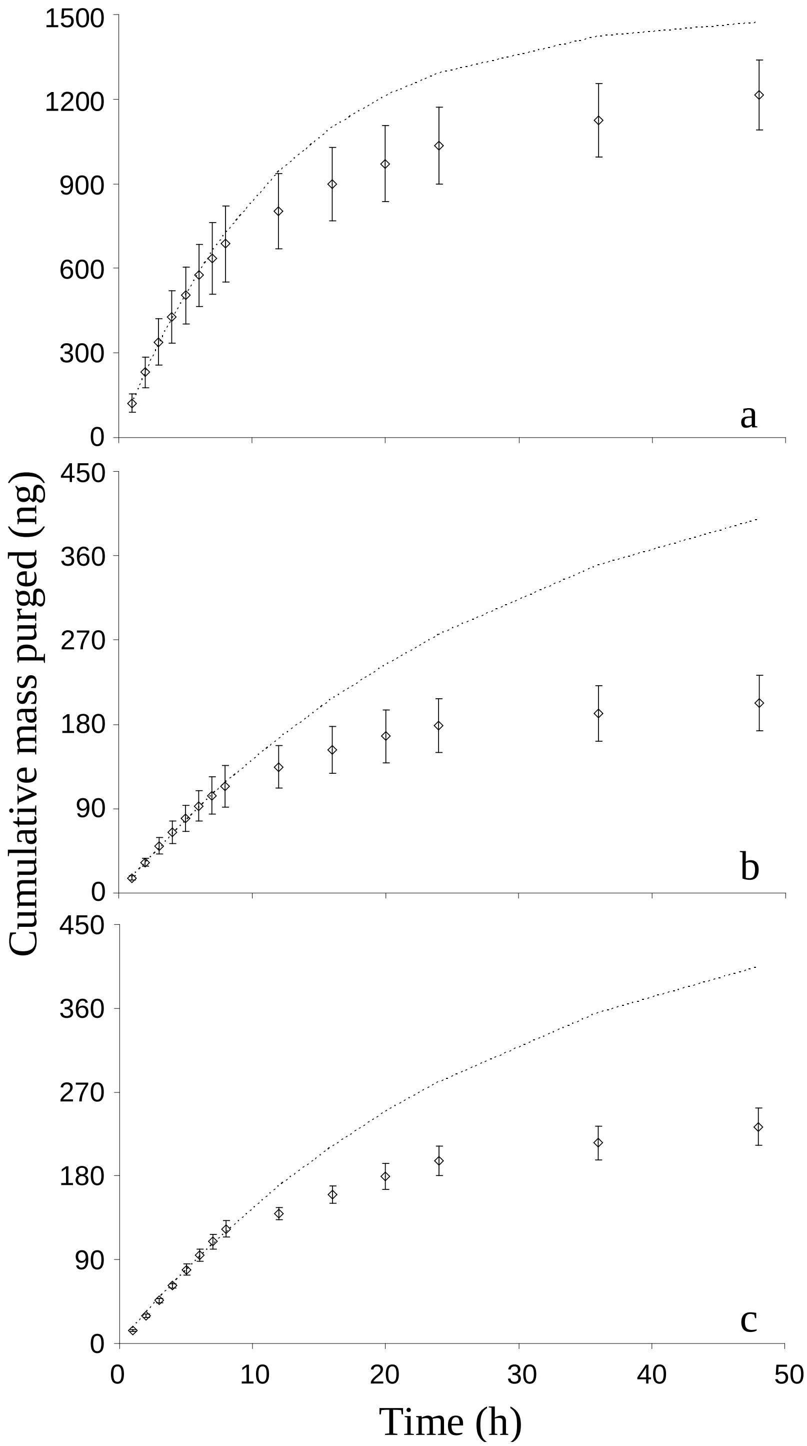

Fig. 3: Typical gas sparging cumulative mass sparged over 48 h for a single experiment including three spargers. Theoretical mass sparged (dotted lines) found using eq. 2 and the volatilization rate found in Fig. 2. (a) TeCB; (b) PeCB; (c) HCB.

Both the statistical analysis and graphical examination of data indicate that the second assumption of the gas sparger technique was invalidated over longer sparging trials. This deviation is explained by considering that during equilibration chemical partitioned to sparger glass surfaces and the release of this material from glass surfaces occurs at a slower rate than volatilization of freely dissolved chemical. Sorption to sparger or vessel surfaces has been observed for many HOCs (Brachet et al., 2005; ten Hulscher et al., 2006; Qian et al., 2011). Unfortunately, despite observing this sorption behaviour, many authors used these materials without correction, leading to potentially erroneous published HLCs among other physicochemical parameters (Brachet et al., 2005, Qian et al., 2011).

Despite sorption to sparger walls, HLC can be determined using the initial phase of the sparging where release from bound sources would be minimal. The k_v rate is anticipated to be dependent on the freely-dissolved chemical during initial sparging until freely dissolved chemical becomes depleted. In the present set of experiments, depletion of freely dissolved chemical occurred as quickly as 6 h following sparging even though this fraction only contributed between 30-50% of the total chemical added to the system.

4.2.Henry's law constants

Calculated HLCs are shown in Table 2 along with reference value ranges found in the literature. HLCs of all three chlorobenzenes were similar, ranging from 29.9–56.5 Pa m^3 mol^{-1}. In comparison to literature values, TeCB in the current study (56.5 Pa m^3 mol^{-1}) falls in the middle of reference ranges for all isomers reported elsewhere. The reference range for the isomers was quite large, spanning an order of magnitude (Table 2). PeCB of the current study was approximately two times lower than measured literature values and the Final Adjusted Value (FAV) of 72 Pa m^3 mol^{-1} calculated by an internally consistent set of physical-chemical property data (Shen and Wania, 2005). Numerous HCB HLCs have been reported in the literature using various measurement techniques (Table 2). The current HCB value of 29.9 Pa m^3 mol^{-1} agrees well with three other gas sparging-type results (35 Pa m^3 mol^{-1}, Jantunen and Bidleman, 2006; 41 Pa m^3 mol^{-1}, ten Hulscher et al., 1992; 49 Pa m^3 mol^{-1}, Oliver et al., 1985), a wetted wall column (24 Pa m^3 mol^{-1}, Altschuh et al., 1999), and a closed system (26 Pa m^3 mol^{-1}, Hansen et al., 1993). Despite being similar to many studies, the current result is much lower than two other gas sparging-type results (130 Pa m^3 mol^{-1}, Atlas et al, 1982; 170 Pa m^3 mol^{-1}, Warner et al., 1987) and the FAV (65 Pa m^3 mol^{-1}, Shen and Wania, 2005).

Calculation of HLCs is of utmost importance to their subsequent use in the determination of partitioning behaviours and environmental fates. Inaccurate determination of HLC may lead to erroneous determination of potential transfer of chemicals throughout various environments (including MWTPs) and lead to inaccuracies in the prediction of compound fates. Gas sparging has been used, since first introduced by Leroi et al., (1977), to measure HLCs of numerous chemicals, including many chlorobenzenes (ten Hulscher et al., 1992). Recently, the gas sparging technique has been criticized due to the potential for compounds to adsorb to gas bubbles and release to the gas phase when bursting (Shunthirasingham et al., 2007). This phenomenon is not accounted for in the gas sparging theory and has lead to potentially high biased results. Given the size of the current compounds' size, it was suggested that adsorption may not be a concern since it occurs more readily for larger compounds. Additionally, the current results fall within or are slightly lower than published results, thus conflicting with the

Table 2: Summary of Henry's law constants calculated using initial slope method from gas sparging results and comparison literature values.

		H (Pa m^3 mol^{-1})			
chemical	**no. of spargers**	**avg.**	**range**	**SE**	**reference range**
TeCB	15	56.5	37.9 – 82.7	3.0	12 – 110[a,b,c,d]
PeCB	15	33.3	16.9 – 56.5	3.1	59 – 85[a,c,d,e]
HCB	15	29.9	16.4 – 51.4	2.8	35 – 170[a,c,d,e, f,g,h,i,j]

[a] Weast, 1972; [b] Mackay et al., 1981b; [c] Oliver, 1985; [d] ten Hulscher et al., 1992; [e] Shen et al., 2005; [f] Warner et al., 1987; [g] Atlas et al., 1982; [h] Jantunen et al., 2006; [i] Hansen et al., 1993; [j] Altschuh et al., 1999.

Note: TeCB values include all isomers.

high biased consideration. Extrapolation of the current methodology to other compounds should take potential adsorption to bubbles into consideration.

4.3.Structure-property relationships

A plot of log HLC versus chlorine number is shown in Fig. 4. Literature values from ten Hulscher et al. (1992) and Oliver (1985) are included for comparison to the current study. Log HLC markedly decreases with increasing chlorine number for all studies. Despite the strong relationship between HLCs and chlorine number, there is variability among isomers of constant chlorine number; a similar trend has been found for PCBs and has been explained by substitution patterns of the chlorine atoms (Burkhard et al., 1985; Dunnivant et al., 1988; Brunner et al., 1990). Correlations between log HLC and chlorine number (#Cl), total molecular surface area (TSA), and molecular weight (MW) all exhibit similar trends due to the inherent correlation between each of these values. Predictive equations using the entire data set can be derived for each parameter.

$$\log \mathrm{HLC} = 1.5523 - 0.1659(\#\mathrm{Cl}) \qquad R^2 = 0.65 \qquad (3)$$

$$\log \mathrm{HLC} = 3.0549 - 0.0141(\mathrm{TSA}) \qquad R^2 = 0.65 \qquad (4)$$

$$\log \mathrm{HLC} = 1.8208 - 0.0044(\mathrm{MW}) \qquad R^2 = 0.66 \qquad (5)$$

Linear relationships for the entire data set improve markedly when the average isomer log HLC values are used; as well, improvements occur when each study is addressed independently. Interestingly, when studies are separated trend lines are parallel to each other (and have $R^2 \geq 0.80$); this indicates that the trends are similar but are reliant upon the variability of study-dependent measured HLCs. As a caveat to using calculated values, H values determined from vapour pressure and solubility in Weast (1972) do not

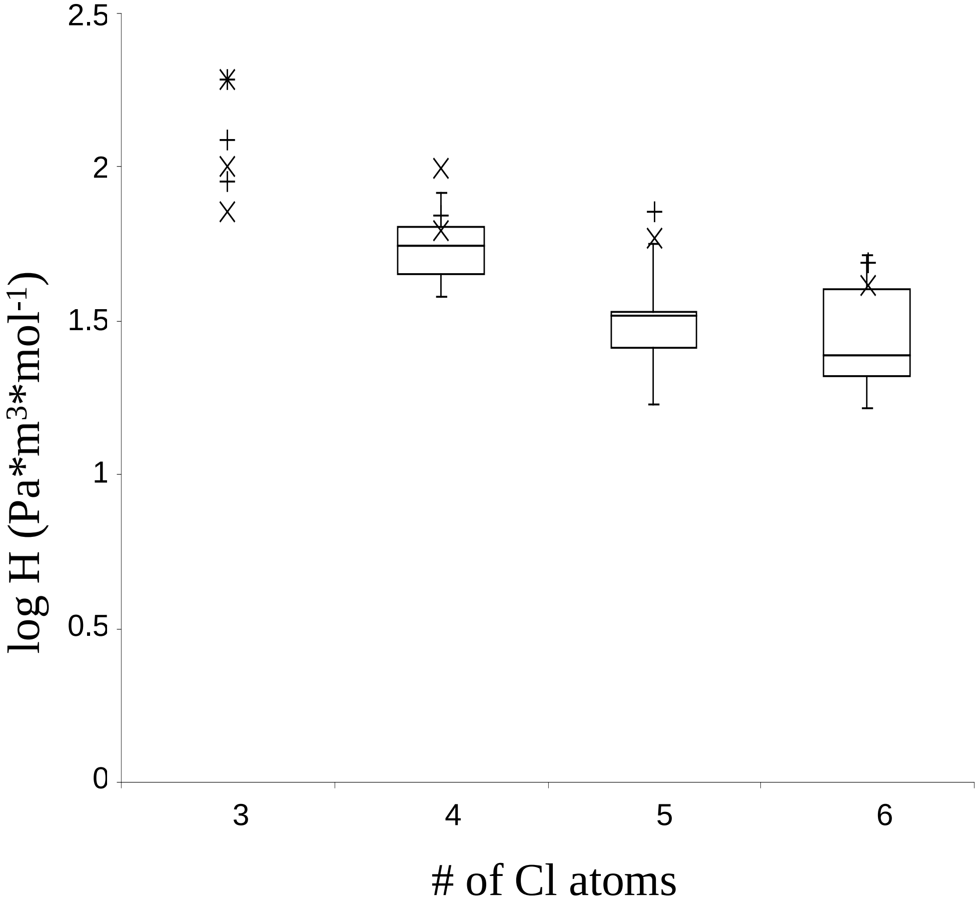

Fig. 4: Dependence of log H values on the number of chlorines (chlorobenzenes). Current study data represented by box and whisker plots. (+) ten Hulscher et al. (1992); (X) Oliver et al. (1985).

follow any of the relationships developed herein with log HLCs of 1.09, 0.93, and 1.14 for TeCB, PeCB, and HCB, respectively.

5. Conclusions

Recently adsorption of analytes onto sampling vessels has become a consideration in calculation of HLC and has subsequently led to questioning of the validity of published data for nonpolar compounds which have not considered adsorption potential (Brachet et al., 2005). Further, Jantunen and Bidleman (2006) expressed the need for validation of differences in measurement techniques and methodologies which may be responsible for observed variations in values and large uncertainty. Current research, including this study, has aimed to broaden the understanding of adsorption in experimental vessels (Qian et al., 2011). This study demonstrated that adsorption of chlorobenzenes to glassware surfaces of the sparger caused a significant reduction in the freely dissolved chemical concentration, with depletion of the freely dissolved fraction occurring after approximately 6 h of sparging. Following this depletion, apparent k_v values decreased in two subsequent stages until glass/water desorption became the rate limiting step for chemical release from the sparger. These artefacts are best evaluated through use of high resolution sampling during the sparger experiment and by verifying mass balance of cumulative mass of chemical released. Unfortunately, many previous gas sparging-type studies were unable to assess these artefacts due to poor sampling resolution and/or minimal sparging duration to verify mass balance (ten Hulscher et al., 1992; Drouillard et al., 1998; Brachet et al., 2005; Jantunen and Bidleman, 2006). Without critical consideration of these parameters the validity of HLCs for these studies may contain technique biases related to glassware sorptive artefacts leading to biased HLCs under the experimental conditions of study. Considering the robust replication of the current study, the HLCs determined from the present research were considered accurate and are to be further used to facilitate understanding of chemical partitioning in dissolved organic matter from MWTP matrices in subsequent research.

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CHAPTER 4

Characterization of cross-flow ultrafiltration fractionated primary sewage effluents using UV_{280} absorbance and ^1H NMR.

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1. Introduction

The movement of chemicals through a municipal wastewater treatment plant (MWTP), both during treatment and into final effluents and sludges, is important in transport of these chemicals of concern (CHC) into receiving environments. An important aspect of this transport process is partitioning of these CHCs to various size fractions of organic matter. Of current interest are the smallest fractions, colloidal organic matter represented by colloidal organic carbon (COC), which appear in all MWTP flows and have not been widely researched. CHCs partitioned to colloids can have several implications for the MWTP process including increased mass transfer from the primary to secondary stage and reduced accessibility of CHCs to loss processes including volatilization and degradation pathways. Partitioning to colloids in the treated effluent exiting the secondary biological stage could further increase the mass of CHCs surviving the treatment process and entering receiving water bodies. This is of concern both for the aquatic environment and human exposure via drinking water.

Very limited studies have attempted to study the ability of CHCs to partition to COC within a MWTP. Also, the distinction between various organic fractions including suspended, colloidal, and truly-dissolved (COC unable to bind specific CHCs) phases has been inconsistent. Literature values for the lower cut-off of suspended solids or particulate organic carbon filters range from 0.45 – 1.5 µm (Tchobanoglous et al., 1991; Vaillant et al., 1999; Holbrook et al., 2004; Shon et al., 2006), while the upper cut-off size defining the truly-dissolved phase has been suggested to be 500 – 1000 Da (Backhus et al., 1990; Gustafsson et al., 2001; Backhus et al., 2003; Holbrook et al., 2004). All size fractions have historically been based on filter availability rather than actual COC characteristics. Truly-dissolved OC cannot be strictly determined via filter size since it is reliant on both chemical size and physiochemical properties.

Wastewater treatment efficiency has traditionally been defined via nonspecific factors such as reduction of biochemical oxygen demand (BOD) and suspended solids (SS) (Levine et al., 1985). These simple parameters are inadequate to discern treatability of all the potential constituents found in wastewater (Fig. 1) and CHCs that can include endocrine disrupting chemicals, pharmaceuticals, personal care products, and other historic CHCs (Shon et al., 2006). Treatability of wastewater is strongly dependent on size distributions of organic matter (OM), thus, characterization of OM size distributions is needed for both understanding of processes and in selection of potential treatment techniques (Levine et al., 1985). OM characterization can be accomplished via various techniques (discussed below) and can also be useful for understanding the effect of and correlation with the partitioning behaviour of CHCs to the various COC fractions. These correlations can further be considered in the understanding of MWTP chemical fate and transport where potential environmental loadings can be determined and possible need for mitigation investigated.

Historically, OM size characterization has been accomplished using numerous methods (Fig. 1). Focusing on the ability to investigate the smallest fractions, four techniques are available including flow field flow fractionation, gel filtration chromatography, high pressure liquid chromatography, and filtration. Filtration (separated into typical membrane and ultrafiltration) is a valuable technique since it is the only method in which the sample can be fractionated without sacrificing, allowing further classification of size fractions and determination of partitioning behavior variation

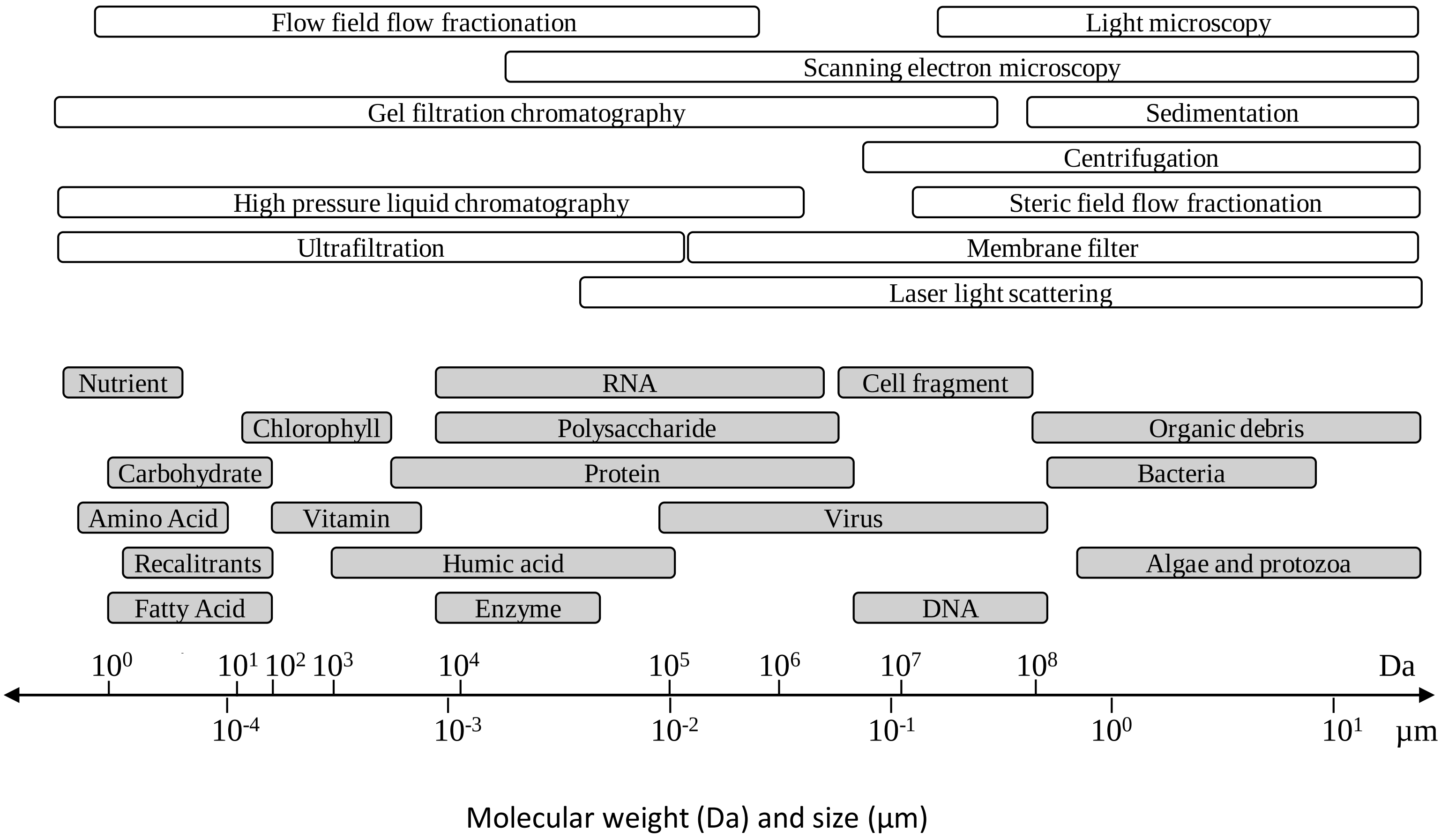

Fig. 1: Typical organic constituents in a MWTP process (bottom shaded cells) and their size ranges. Analytical techniques used to indentify size ranges (top clear cells). Adapted from Levine et al. (1985) and Shon et al. (2006).

between fractions. Ultrafiltration in the laboratory may be accomplished via traditional stirred-cells and the more recently developed membrane capsules based on cross-flow technique. Unfortunately direct comparison of the two techniques is lacking in the literature making direct comparisons of filtered size fractions potentially erroneous (Becht et al., 2008). However cross-flow filtration capsules have much larger filter surface area which increases filtration capacity which is needed to generate the wastewater volume required for partitioning experiments. Additionally, cross-flow filtration is a better representation of membrane systems used at commercial and industrial scales.

A few characterization methods have been used previously for correlation of CHC binding to natural organic matter (Gauthier et al., 1987; Backhus et al., 1990; Chin et al., 1992; Gustafsson et al., 1997; Chin et al., 1997; Laor et al., 2002). Common characterization techniques include XAD fractionation, elemental analysis, and UV absorbance. More recently, some studies have attempted to extend these correlations to MWTP COCs (Perminova et al., 1999; Vaillant et al., 1999; Holbrook et al., 2004; Ilani et al., 2005; Borisover et al., 2006; Worms et al., 2010; Navalon et al., 2011). The value of XAD fractionation has recently been questioned due to inconsistencies in methods and results indicating lack of true separation of fractions (Labanowski et al., 2011; Navalon et al. 2011). Elemental analysis has been used previously to correlate molecular ratios to binding efficiency, however, has shown to have poor correlation in comparison to other available methods (Perminova et al., 1999). UV absorbance is an indicator of aromaticity which has been shown to correlate well with partitioning of various CHCs (Gauthier et al., 1987; Gustafsson et al., 1997; Perminova et al., 1999; Holbrook et al., 2004).

Nuclear magnetic resonance (NMR) was recently identified as an ‘emerging detection technique’ for environmental analysis by Koester et al. (2003). Despite some criticism of the technique as inaccessible to researchers (Gustafsson et al., 2001; Holbrook et al., 2004), advances in sensitivity of instruments has made the technique viable (Koester et al., 2003) and it has been investigated over the past decade for environmental analysis (Koester et al., 2005). Proton NMR or ^{1}H NMR is a common application of the NMR technique which uses hydrogen nuclei to determine molecular structure.

^{1}H NMR has been sparsely used for MWTP samples and results have exhibited high variability (Fujita et al., 1996; Navalon et al., 2011). Aldrich humic acid (AHA) ^{1}H NMR has been used historically for comparison to colloidal organic matter and serves as a good indicator of proper NMR experimental robustness. Results of AHA ^{1}H NMR spectra for two studies show that overall the spectra exhibit similar trends including significant peaks in the 0–3 ppm range, no peaks after 9 ppm, and a residual water peak at 4.7 ppm. However, the results exhibit that despite improvements in NMR sensitivity the spectral resolution is poor and the sample preparation and results interpretation are questionable. Although peaks are found in the 0–3 ppm and 6–9 ppm ranges, they are inconsistent even within a single study (Hinedi et al., 1997). Additionally, the water peak is poorly suppressed in both studies. Actual MWTP sample ^{1}H NMR results were recently shown by Navalon et al. (2011) for DAX8 and XAD4 fractionated samples (Fig. 3). However, Navalon et al. (2011) question the validity of the fractionation method used due to the larger overlap of spectra exhibited by fractions that are assumed to be mutually exclusive. These various issues may in part explain its

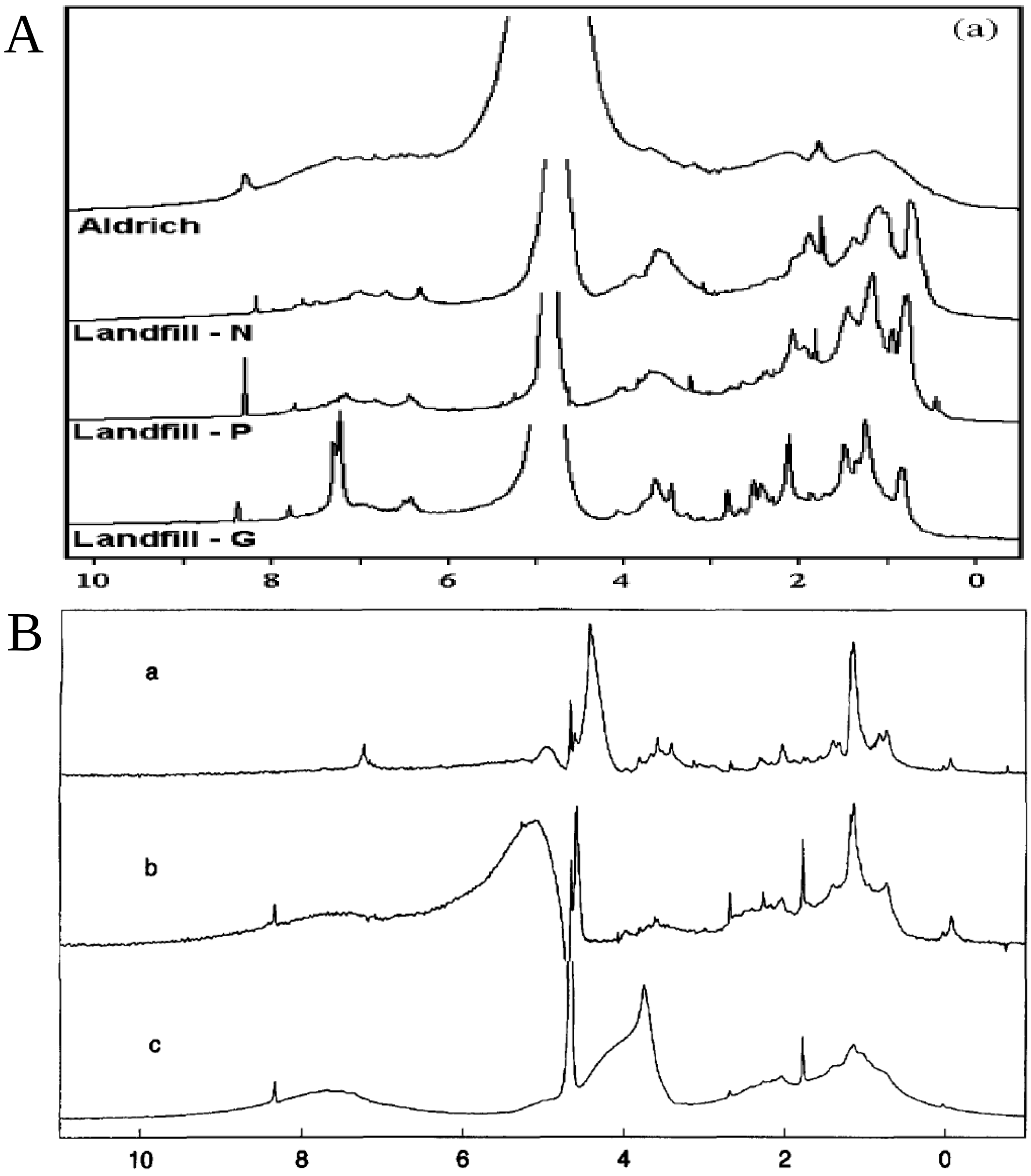

Fig. 2: ^{1}H NMR spectra of AHA. (A) passing 0.45 µm filter various sample from Kang et al. (2002); (B) molecular weight fractionated sample after 0.45 µm filter from Hinedi et al. (1997). (a) 1000 amu, (b) 8000 amu, (c) unfractionated.

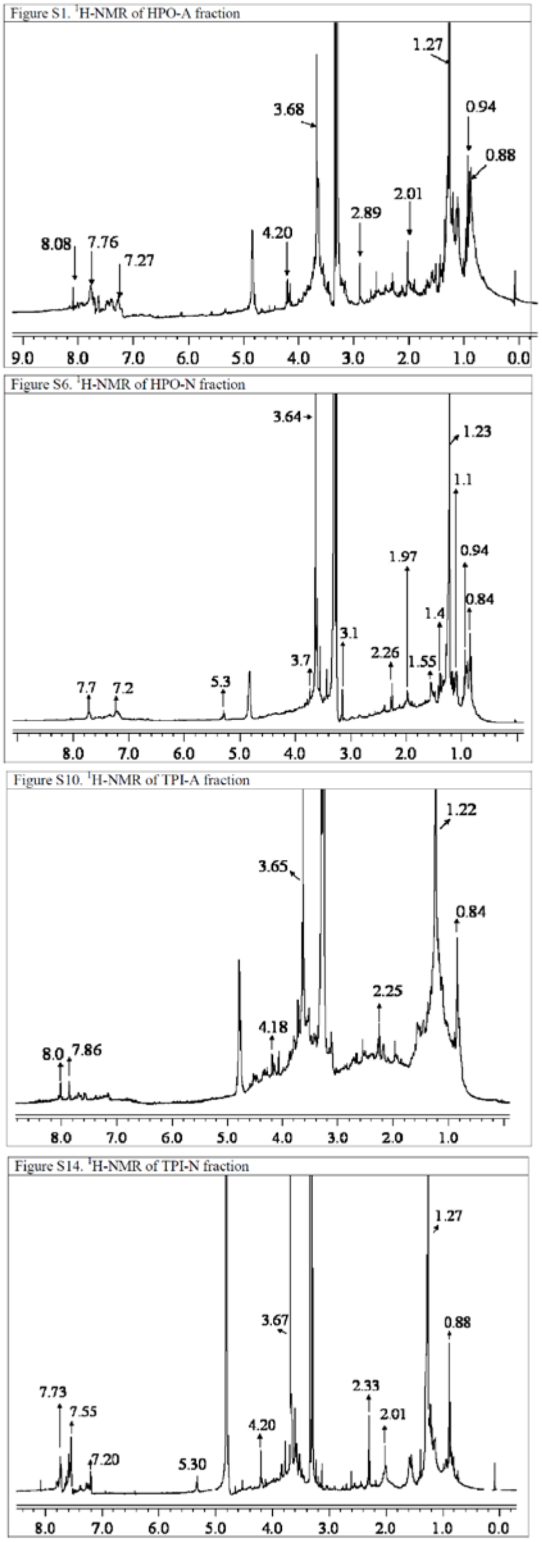
Figure S1. ^{1}H-NMR of HPO-A fraction

Figure S6. ^{1}H-NMR of HPO-N fraction

Figure S10. ^{1}H-NMR of TPI-A fraction

Figure S14. ^{1}H-NMR of TPI-N fraction

Fig. 3: ^{1}H NMR spectra of wastewater effluents separated using DAX8 and XAD4 fractions taken from Navalon et al. (2011).

limited application in wastewater analysis and exhibit the need for more robust NMR experiments.

The objectives of this study were (1) to develop a repeatable and robust size fractionation technique for MWTP primary effluents; (2) develop a ^{1}H NMR sample preparation method to simplify sample work-up, increase sensitivity, and reduce duration of instrumental usage; (3) further characterization of size fractionated OM using UV absorbance and developed technique for ^{1}H NMR analysis; (4) to increase the understanding of OM distribution and characteristics and the potential partitioning of CHCs to various size fractions. The fraction passing a 1.5 µm filter was considered to include the colloidal organic matter examined in the current study. This is due to the use of this filter size in MWTP standard methods as the delineation between suspended and dissolved solids. Aldrich humic acid (AHA) samples are used for comparison since they are widely used as a standard reference for colloidal organic matter. Comparison of AHA to NOM, including MWTP OM is discussed to determine the efficacy of using AHA as a surrogate for MWTP OM.

2. Methods

2.1.Wastewater sampling

Samples were taken from Little River Pollution Control Plant (LRPCP) in Windsor, Ontario, Canada. The plant serves the eastern portion of the City of Windsor and the surrounding municipalities of Tecumseh, St. Clair Beach and Sandwich South, and has two parallel and similar activated sludge-type secondary wastewater treatment systems with a combined design capacity of 60 000 m^{3} d^{-1}. Approximately 10 L grab samples were collected at the primary sedimentation tank using a 25 L pre-cleaned container during 2009 – 2011 under normal dry weather conditions. Samples were transported to the laboratory within one hour of collection and treated with ca. 100 mg L^{-1} sodium azide to inhibit microbial degradation.

2.2.Humic acid solution preparation

An ca. 2 g L^{-1} concentration of humic acid sodium salt (Sigma Aldrich) was dissolved in MilliQ water, stirred using a Teflon stir bar for 1 h and filtered using a 1.5 µm glass fibre filter (Whatman 934AH). A stock buffer solution was prepared by dissolving 3.4 g of KH_2PO_4 and 3.5 g of K_2HPO_4 in 1 L of MilliQ water. The humic acid solution was buffered to a pH of 6.7 and 100 mg of sodium azide was added to prevent potential degradation.

2.3.Filtration

Samples were filtered through a series of gravimetric filters in the following order: 1.5 µm glass fiber filters (Whatman 934AH); 1.1 µm glass fiber filters (VWR Grade 693); 0.45 µm cellulose nitrate filters (Whatman Type WCN); 0.22 µm cellulose nitrate filters (Fisher Scientific). All filters were conditioned with distilled water (ca. 50 mL) and filtrate from the previous filter (ca. 50 mL) prior to sample collection. The 0.22 µm sample (ca. 3 L) was further fractionated using Minimate 1 kDa, 30 kDa, and 100 kDa tangential flow filtration capsules (Pall Life Sciences) described in Section 2.4.

2.4.Cross-flow ultrafiltration (CFUF) system

The CFUF system consisted of parallel flow streams to Minimate tangential flow filtration (TFF) capsules (1, 30, and 100 kDa; Pall Scientific) with Omega ultrafiltration membranes which are low protein-binding, modified polyethersulfone membrane (effective surface area 50 cm^2) contained in a polypropylene outer housing and a Masterflex L/S peristaltic pump (Cole Parmer). The pump, pressure gauges (feed and retentate ports), and individual filters were connected with 3.2 mm ID silicone tubing. Sampling mode (retentate returned to feed flasks) was used to process the samples under the following conditions: feed inlet pressure 100–140 kPa, retentate outlet pressure < 70 kPa psi, retentate flow rate 30 – 40 mL min^{-1}, and permeate flow rate variable according to filter pore size. Each TFF capsule was cleaned prior to and after experimental use with 200 mL 0.1 N NaOH in recirculation mode for 2 h. After cleaning, the filter was conditioned using 200 mL MilliQ water through both retentate and filtrate ports. 50 mL of sample filtrate was rejected prior to collection. Cleaned capsules were tested for performance degradation using the normalized water permeability (NWP) section of the included manual. Filters used passed the NWP test on each sampling occasion allowing for continued reuse.

To determine filter membrane performance, a mass balance was performed on each TFF membrane prior and post use (blank analysis). Each filter processed 150 mL of 0.22 µm filtrate, with 100 mL passing the filter (filtrate) and 50 mL in the feed (retentate). COC measurements were taken for each flow and a mass balance performed to determine recovery.

2.5. Organic carbon measurement

Aliquots of each filter fraction were quantified for total carbon (TC) and total inorganic carbon (TIC) using a Shimadzu TOC-5000 Analyzer (Shimadzu Scientific Instruments). Each sample was run five times and the arithmetic average was taken for further calculations. Total organic carbon (TOC) was found using the following equation: TOC = TC – TIC. TOC is equivalent to the COC parameter.

2.6.UV absorbance measurement and molar extinction coefficient

Aliquots of each filter fraction were quantified for UV absorbance at 280 nm using a Varian Cary 50 UV-vis spectrophotometer (Agilent Inc.). Three measurements were taken for each aliquot and the arithmetic mean was used for further calculations. Molar extinction coefficients (e_{280}) for each size fraction were calculated by dividing the absorbance by the COC concentration.

2.7.^{1}H NMR sample preparation and measurement

All NMR methods may be used to quantify dilute samples using multiple sampling scans; however, using multiple scans is time consuming leading to increased cost for instrument usage (or fewer sample experiments). To shorten ^{1}H NMR experimental duration to less than one hour, fractions were concentrated prior to preparation for NMR experiments. Aliquots of 50 mL for each size fraction were placed in 100 mL crucibles and evaporated in an 80 °C oven. Samples were mixed regularly to reduce solids drying onto crucible walls. Deuterated water (1 mL) and 1 mg mL^{-1} sodium 2,2-dimethylsilapentane-5-sulphonate (DMSO; 1 mL) were added to a 10 mL volumetric flask. Once the sample evaporated to ca. 5 mL it was transferred to the volumetric flask and distilled water used to rinse the crucible and create a 10 mL final solution for NMR analysis using a Bruker DRX500 NMR spectrometer (Bruker Inc.). Preliminary experiments to determine concentration technique efficiency included 1.5 µm samples in unconcentrated, 10X concentrated, and 20X concentrated treatments. Further experiments included 0.22 µm, and ultrafiltration samples (1, 30, and 100 kDa) concentrated 10X based on preliminary experiment results exhibited settling of COCs in 20X concentrated treatments.

3. Results and Discussion

3.1.Cross-flow ultrafiltration (CFUF)

Results from the overall mass balances are shown in Table 1. Recoveries decreased (88.3% > 85.1% > 77.8%) according to membrane sizes (100 kDa > 30 kDa > 1 kDa). Losses in the current study are reasonable as compared to Wilding et al. (2004) for validation experiments using molecular probes (79–103%), as well as similar to a reverse osmosis fractionation mass balance of 75% by Ma et al. (2001). Evaluation of the operational efficiency of cross-flow ultrafiltration using methods such as molecular probes has been well documented in the literature (Gustafsson et al., 1996; Larsson et al., 2002; Wilding et al., 2004; Dalwadi et al., 2005; Kottelat et al., 2008; Schwalger et al., 2009). Given the variety of CFUF systems and applications, it is suggested that the performance of the system be evaluated prior to use for molecular weight cut-off, mass balances, and membrane cleaning efficiency when reused (Buessler et al., 1996; Wilding et al., 2004). The current molecular weight cut-offs of the TFF membranes were considered accurate given previous verification experimental results of the current membranes (Dalwadi et al., 2005; Schwalger et al., 2009) and similar membranes (Gustafsson et al., 1996; Larsson et al., 2002; Wilding et al., 2004; Liu et al., 2005; Kottelat et al., 2008); however, it should be noted that similar 1 kDa membranes have shown to have a cut-off closer to 2 kDa (Larsson et al., 2002; Wilding et al., 2004). The current membranes were assessed for COC mass balance and membrane cleaning efficiency only. All membranes had minimal COC concentration post-cleaning in all experiments (MilliQ blanks < 0.5 mg L^{-1}).

3.2.COC fractionation

For clarity, filter sizes are all converted from kDa to µm (using the equation from Shon et al., 2006) for ease of graphing and comparison to other studies (Figs. 4 and 5). Overall, COC sample fractions showed reasonable consistency over the study duration, therefore, it appears that MWTP COC sizes are seasonally stable given the limited sampling regime (Table 2). COC concentrations progressively decreased with each size fraction, starting from 49.7 mg L^{-1} for the 1.5 µm fraction to 33.1 mg L^{-1} for the 0.0005 µm fraction. For comparison, raw measured literature values for various MWTP flows are presented in Fig. 5 using both COC (mg L^{-1}) and equivalent COD (mg L^{-1}) measurements. (using COD = 3*COC, Mara and Horan, 2003). Sophonsiri et al. (2004) also measured a primary effluent, with results similar to the current study in both distribution and magnitude (Fig. 4). Holbrook et al. (2004) measured the mixed-liquor suspended solids, with results varying from the current study in both distribution (in the lowest size fractions) and magnitude. The lower magnitude is expected considering the sample is equivalent to final effluents, which would have a lower COC content.

Table 1: Mass balance analysis of CFUF membranes.

		membrane (kDa)		
flow	units	1	30	100
input	conc (mg L^{-1})	48.3	48.3	48.3
	mass (mg)	7.3	7.3	7.3
filtrate	conc (mg L^{-1})	32.6	37.5	40.1
	mass (mg)	3.3	3.8	4.0
retentate	conc (mg L^{-1})	47.6	40.6	40.1
	mass (mg)	2.4	2.4	2.4
% recovery*		77.8%	85.1%	88.3%

$$^{*}\text{recovery (\%)} = \frac{retentate(mg) + permeate(mg)}{input(mg)}$$

Table 2: Summary of size conversions and COC and AHA size fractions. COC size fractions represent multiple samples with standard error. AHA size fractions represent stock solution.

filter size (passing)	size (µm)* (passing)	COC (mg L^{-1}) avg (SE)	AHA (mg L^{-1}) avg
1.5 µm	1.5	49.7 (3.6)	49.7
1.1 µm	1.1	47.1 (4.4)	47.0
0.45 µm	0.45	44.8 (4.3)	44.0
0.22 µm	0.22	41.9 (4.1)	43.4
100 kDa	0.01	39.3 (3.2)	20.9
30 kDa	0.0015	36.7 (0.8)	5.5
1 kDa	0.0005	33.1 (1.0)	2.3

$^{*}size(\mu m) = \dfrac{0.0001*(Da)^{0.3321}}{2}$ (Shon et al., 2006)

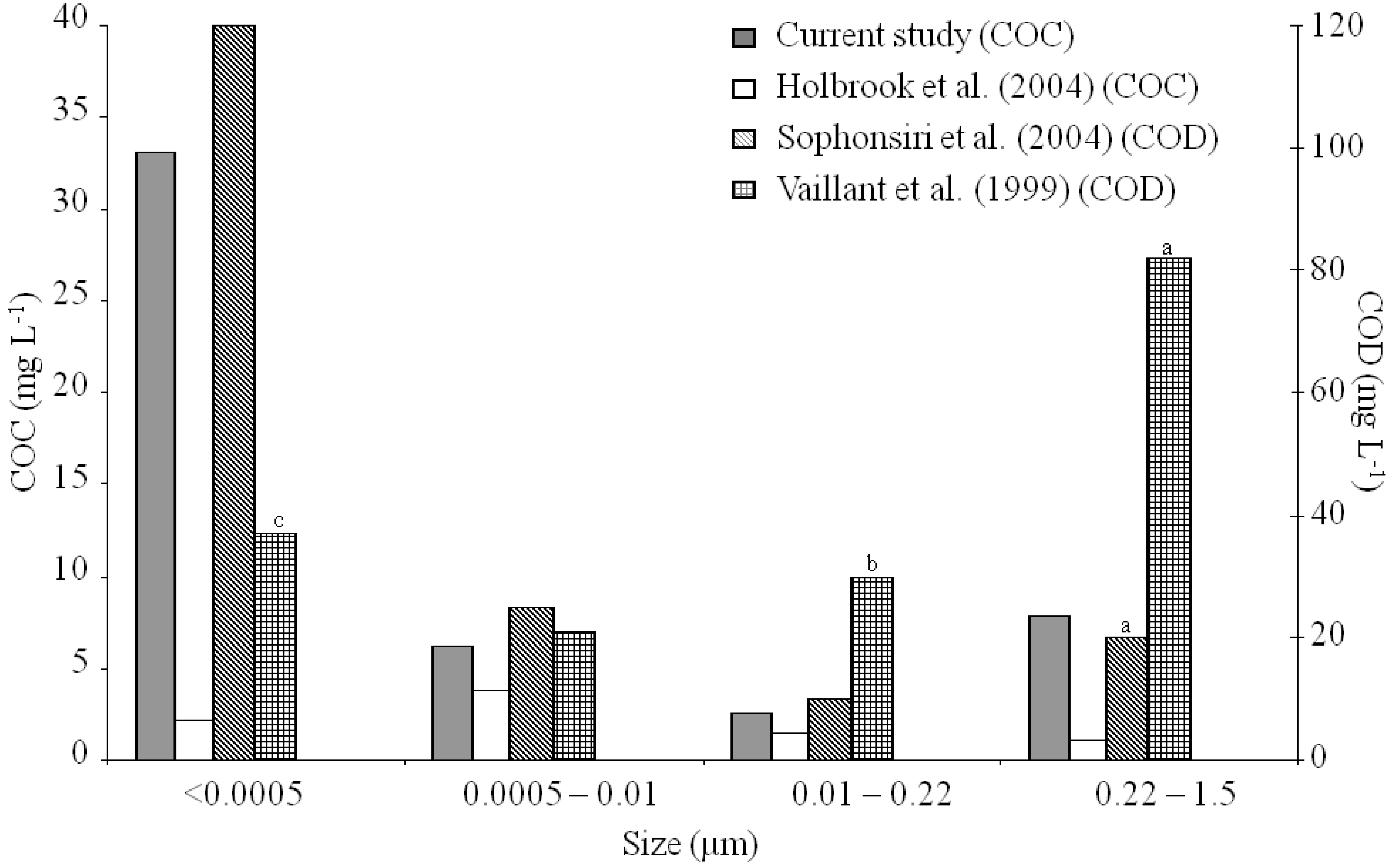

Fig. 4: Mass fractions of fractionated sample: (i) Current study – primary effluent; (ii) Holbrook – MLSS; (iii) Sophonsiri – primary effluent; (iv) Vaillant – influent. [a]1.2 μm filter; [b]0.1 μm upper limit; [c]0.0011 μm filter.

However, Holbrook et al. (2004) used stirred-cell filtration, which may lead to poor passing of smaller size fractions (Dalwadi et al., 2005). Therefore the results for their lowest size fractions were grouped for the current comparison (see discussion below; Fig. 5). The final comparison is Valliant et al. (1999) influents, which have a greater representation of the larger fraction. AHA concentrations exhibited a less progressive decrease, with 58% of the mass concentrated in the > 0.22 µm size fraction and only 12% of the mass in the < 0.0015 µm size fraction. Kang et al. (2002) found a similar distribution for AHA samples with 7% of mass found in the < 0.001 µm size fraction. Clearly the size distribution of AHA is markedly different than the current MWTP primary effluents.

Comparison between studies is difficult considering the vast differences in filter sizes used amongst researchers (Fig. 4). To mitigate these differences and allow a better comparison, percent passing was considered for the fractionated sizes (Fig. 5). The additional benefit of percent passing is that COD measurements conversion is unnecessary. Although used regularly for sieve series of larger particles, to our knowledge this method has not been used for ultrafiltration/filtration analysis. As shown in the first three Figures 5a-c, the regression lines are remarkably close in both slope and intercept. Using the regression line equations, the 0.0005 µm fractions are 67.7%, 69.3%, and 66.4% for the current study, Sophonsiri et al. (2004), and Holbrook et al. (2004), respectively. Using an analysis of covariance (ANCOVA), these slopes are found to be statistically similar ($p > 0.05$; ANCOVA). These excellent similarities exhibit the consistency in size distributions between MWTP system COC fractions both in primary effluents and MLSS (essentially final effluents), with the only differences occurring in magnitude, as would be expected after the aeration process. Compared to the current study Figures 5d-f are statistically different (d: $p < 0.05$; e: $p < 0.10$; f: $p < 0.10$; ANCOVA).

Aldrich humic acids have been used historically as a surrogate humic acid for comparison with NOM and COC (Fig. 5). The linear regression results in only 9.9% in the lowest size fraction; this result confirms that AHA should only be used for method comparison and does not correlate well with MWTP COC. The influent sample E (Vaillant et al., 1999) linear regression results in 2.8% in the lowest fraction (Fig. 5). As mentioned previously, much of the larger size fraction may be lost in the primary sedimentation, thus making direct comparison to the current study erroneous. The final sample of secondary influents linear regression results in 28.9% in the lowest fraction (Fig. 5f). However, filters used by Manka et al. (1982) for this fraction differed from more current studies and have not been thoroughly evaluated via molecular probes.

The 0.0005 µm fraction is of most interest currently, since this it has been used most often as the truly-dissolved cut-off in the literature (Backhus et al., 1990; Gustafsson et al., 2001; Backhus et al., 2003; Holbrook et al., 2004) as well as being the smallest pore size cross-flow ultrafiltration capsule currently available. The fraction passing 0.0005 µm in the three studies of interest (Fig. 5a-c) are close to 70%, making this lowest size fraction the dominant proportion of the colloidal phase in municipal wastewaters. Given this dominance, and a recent study exhibiting potential sorption capacity of this fraction (see Chapter 6), this fraction must be considered for further investigation.

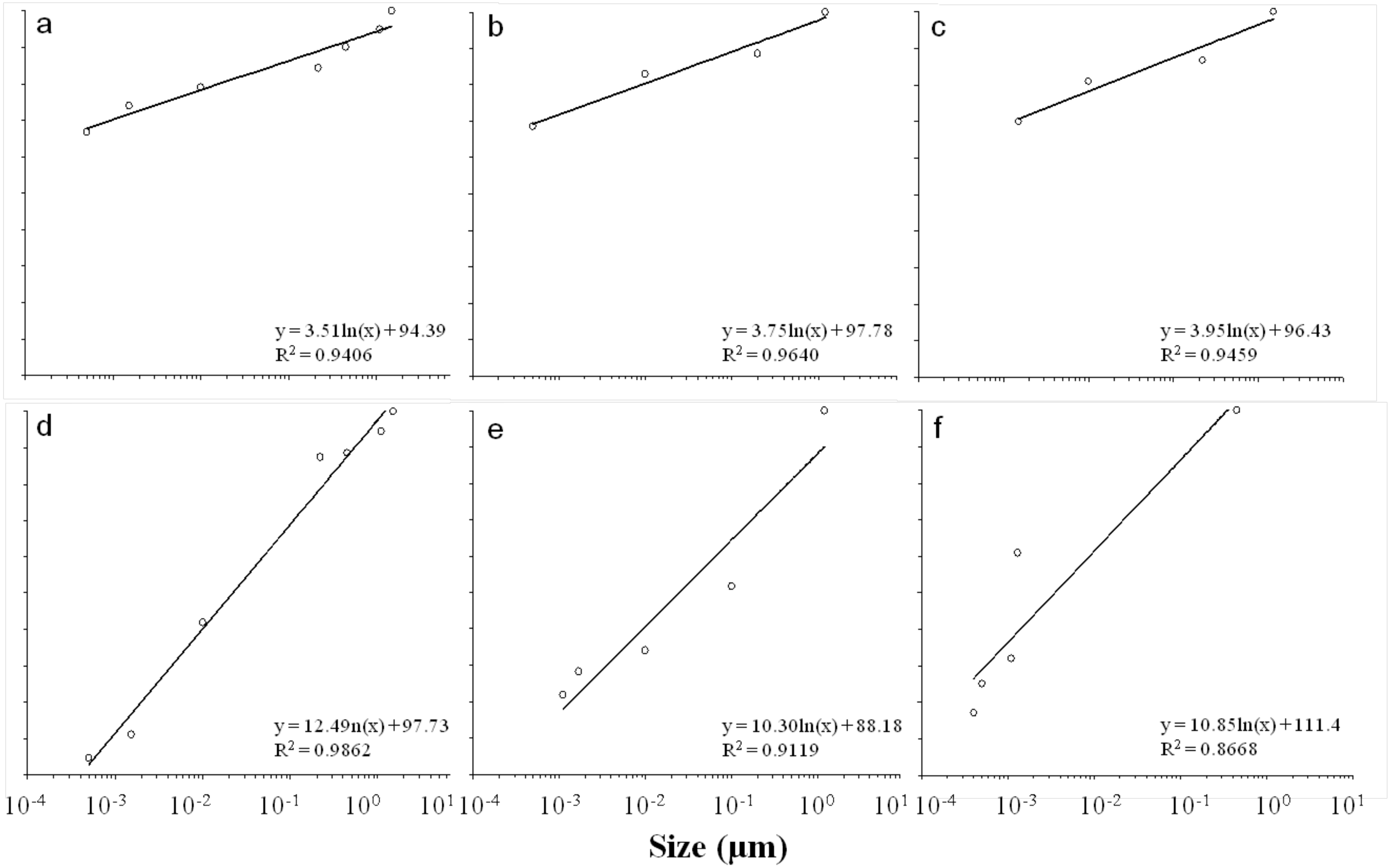

Fig. 5: Percent passing of filtration fractions of various COC and AHA samples. (a) Current study primary effluent; (b) Sophonsiri et al. (2004) primary effluents; (c) Holbrook et al. (2004) MLSS; (d) Current study AHA; (e) Vaillant et al. (1999) influents; (f) Manka et al. (1982) secondary effluents.

3.3.UV absorbance and molar extinction coefficient

Molar extinction coefficients (e_{280}) for COC and AHA are shown in Fig. 6. The linear regression between e_{280} and logarithmic fraction size exhibits excellent linearity ($R^2 = 0.977$) for COC, while no correlation between e_{280} and AHA was found. The e_{280} coefficients are within literature ranges for freshwater, marine, and MWTP studies (Chin et al., 1994; Gustafsson et al., 2001; Holbrook et al. 2004). Correlations between UV absorbance and partitioning of HOCs have been shown in many environments (Gauthier et al., 1987; Chin et al., 1997; Perminova et al., 1999; Gustafsson et al., 2001; Holbrook et al., 2004). The e_{280} is considered a descriptor of sample aromaticity, which has been positively correlated to sorption. Holbrook et al. (2004) used a similar fractionation method as the current study and also measured e_{280} values. However, unlike the current study, their e_{280} values showed no linearity. Alternatively, Chin et al. (1994) found a direct correlation between aromaticity and molecular weight for humic acids and Imai et al., (2002) found a correlation between molecular weight and UV absorbance for effluent samples using UV absorbance at 260 nm. Differences between AHA and COC are shown by the lack of correlation between AHA e_{280} and size fractions (Fig. 6) reiterating the inaccuracy of using AHA as a surrogate to COCs in experimental study.

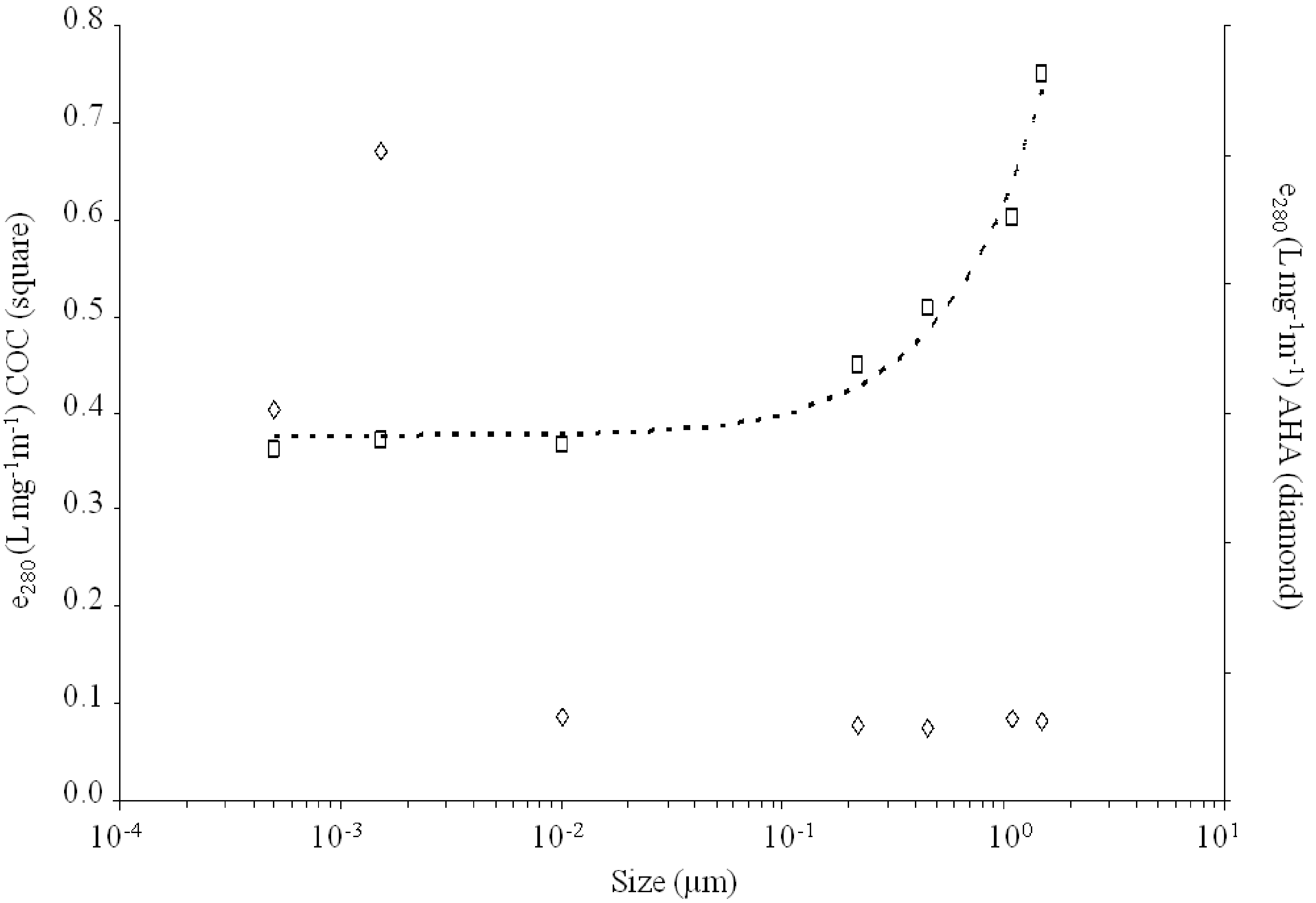

Fig. 6: Molar extinction coefficients (e280) of COC and AHA. COC values are averages from multiple samples. A single AHA standard was used for all experiments.

3.4.^{1}H NMR – Method validation

Unconcentrated (Fig. 7A) and resuspended (Fig. 7C) COC spectra indicate similar overall peaks. Dried and reconstituted NMR spectra peaks became very broad and less precise (Fig.7C). The broad peaks lead to poorer resolution and inability to integrate individual peaks, thus allow the researcher to only report segment information which has limited use in further understanding of partitioning behaviour (Table 3). Using the current method of analysis, unconcentrated samples (Fig. 7A) may be used directly for NMR analysis thus limiting sample work up and potential changes to the sample matrix caused by completely drying the sample. However, for greater sensitivity NMR experiments must be run for a longer duration for unconcentrated samples.

Unconcentrated spectra (Fig. 7A) correspond well with the concentrated spectra (Fig. 7B) and provide similar resolution as indicated by comparison to the DMS peak at 0 which is equivalent for each spectrum. Using the current method concentration of actual OM MWTP samples up to 10X was considered for further investigation. Samples concentrated further lead to settling of OM due to solubility limitations in water. The validity of the concentration was verified by comparison of ^{1}H NMR spectra for unconcentrated, 10X concentrated, and resuspended experiments exhibiting the same individual peaks and similar relative percentages in each segment (Fig. 7; Table 3). With concentrated samples the sensitivity of NMR experiments is increased allowing for shorter duration NMR experiments.

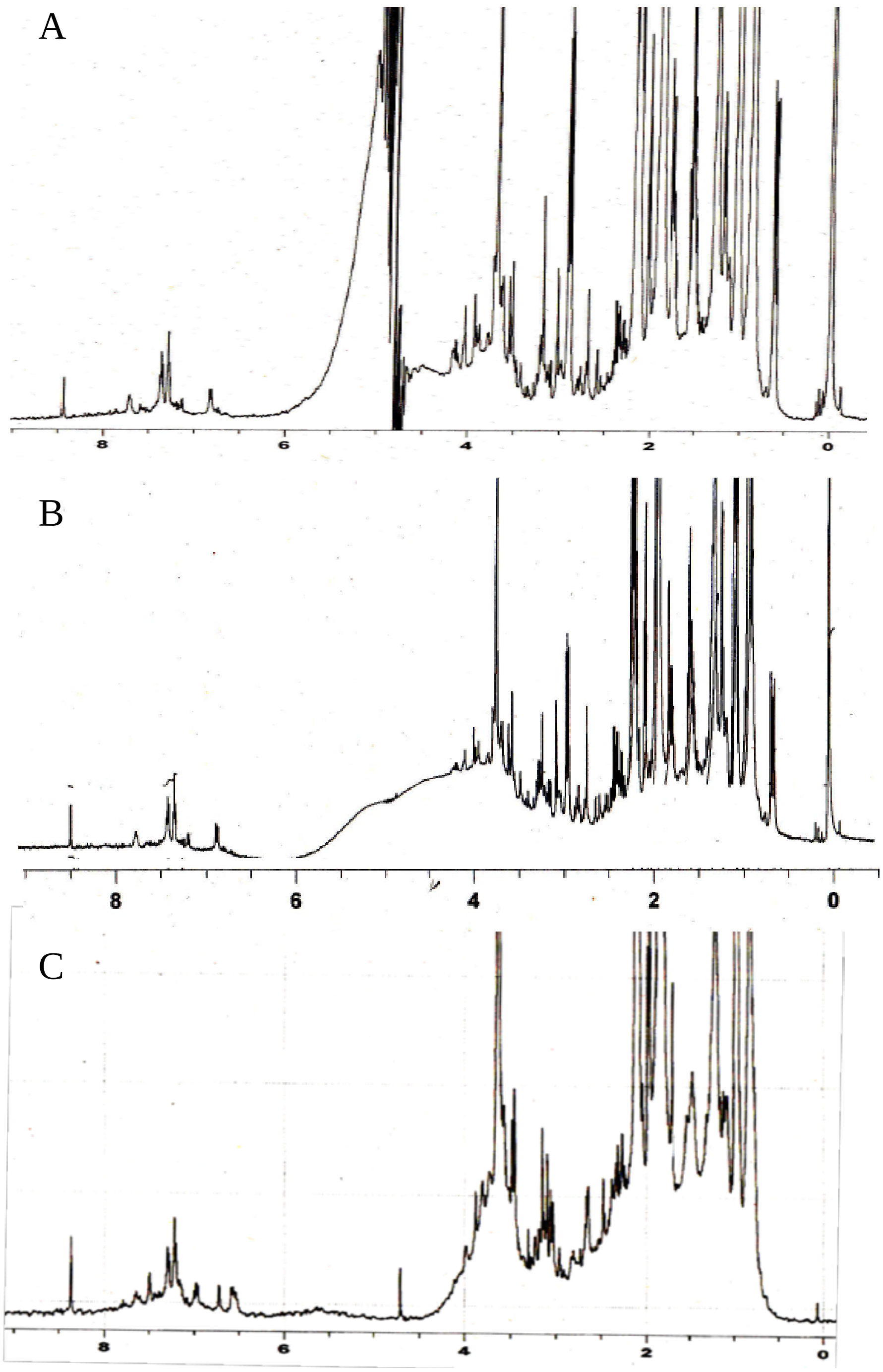

Fig. 7: ^{1}H NMR spectra of effluent samples. (A) unconcentrated; (B) 10X concentrated; (C) dried sample. Standard DMS peak at 0 ppm may be used to scale spectra for quantitative analysis (included in Table 3) and water peak shown at 4.7 ppm.

Table 3: Proportion (ppm) of non-exchangeable hydrogen as determined from ^{1}H NMR spectra for unconcentrated, 10X concentrated, and dried samples.

	relative percentage (%)				
sample	0.5 – 1.9 ppm	1.9 – 3.1 ppm	3.1 – 4.6 ppm	4.6 – 6.0 ppm	6.0 – 9.0 ppm
unconcentrated	35.4	64.6	0	0	0
10X concentrated	24.1	73.1	2.2	0	0.6
dried	31.5	65.0	2.6	0.4	0.5

The current method of sample preparation and liquid-state ^{1}H NMR has not been previously used, however serves as a valuable evolution for sample processing and provides two separate benefits. The first benefit is the ability to use unconcentrated samples directly without sample work-up. The second benefit is the ability to concentrate samples without affecting the sample integrity.

3.5.^{1}H NMR fractions - COC

A representative ^{1}H NMR series of spectra for various fractionated OM are shown in Fig. 8. As indicated, seven individual peaks were determined with area counts relative to the DMS standard at 0 ppm. The spectra in the 4.7 ppm section exhibit no peaks due to water suppression in the processing of the experiment. However, peaks in this section were not shown in the dried spectra which exhibit minimal water peaks due to resuspension in methanol (Fig. 7C) and would not be expected in the concentrated spectra. Of the seven peaks, three areas remain constant throughout the size fractions (0.7, 1.8, 2.9 ppm). The remaining peaks all exhibit decreasing area trends with decreasing size fractions (0.9, 1.0, 2.0, 2.2 ppm). Due to the overlapping nature of the size fractions it would be expected that some peaks would remain constant (indicating peaks of smaller size OM not filtered out) and others would decrease (indicating OM filtered out). Given the ability to define individual peaks and exhibit changes in OM spectra with filter sizes the potential to attribute potential partitioning behaviour based on specific OM characteristics can be realized.

Proportion of peak signals found within each chemical shift region is shown in Table 4. Assignments for each region are aliphatic (0.5–1.9 ppm), neighbour to

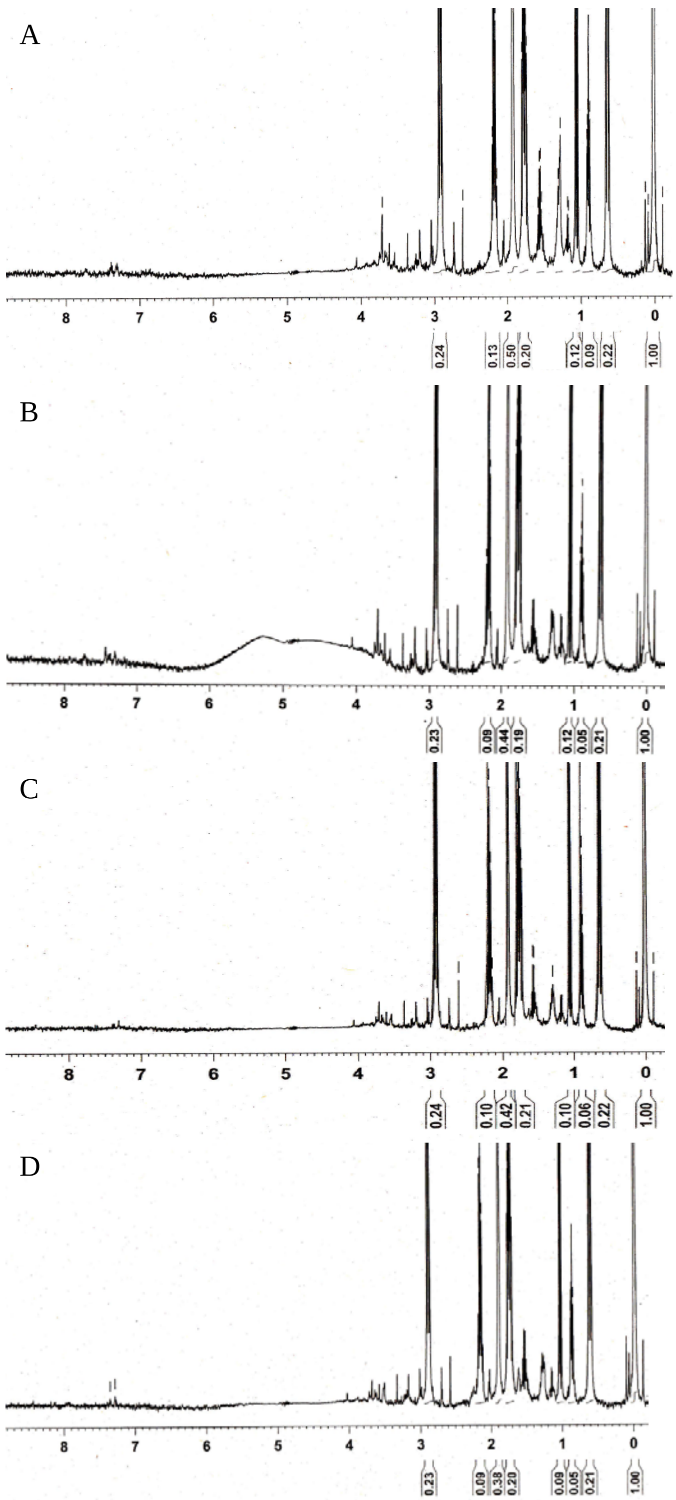

Fig. 8: ^{1}H NMR spectra of various size fractions including: (A) 0.22 µm; (B) 0.01 µm; (C) 0.0015µ m; (D) 0.0005µ m. Peak at 0 ppm represents DMS standard with each sample peak area relative to standard area. Water suppression used at 4.7 ppm.

Table 4: Proportion (ppm) of non-exchangeable hydrogen as determined from ^{1}H NMR spectra using 10X concentrated filter samples.

sample	filter size (passing) (µm)	relative percentage (%) 0.5 – 1.9 ppm	1.9 – 3.1 ppm	3.1 – 4.6 ppm	4.6 – 6.0 ppm	6.0 – 9.0 ppm
WWTP	1.5	24.1	73.1	2.2	0	0.6
	0.22	46.0	54.0	0	0	0
	0.01	33.1	65.9	0	0	1.0
	0.0015	34.5	65.0	0	0	0.5
	0.0005	37.1	62.3	0	0	0.5
AHA	1.5	66.0	34.0	0	0	0

unsaturated groups (1.9–3.1 ppm), O–CH (3.1–4.6), O–CH–O (4.6–6.0 ppm), and aromatics (6.0–9.0 ppm) (Thorn, 1994; Santos et al., 2009; Navalon et al., 2011). The majority of the current signal is found within the first two segments (0.5–1.9 ppm and 1.9–3.1 ppm), with marginal quantities in the final segment (6.0–9.0 ppm). The 0.5–1.9 ppm segment has been identified as fatty acids, lipids or related compounds (Navalon et al. 2011). Although compounds in this region are expected (Fig. 1), the large proportion in this region (ranging from 23.3 – 46.0 %) is higher than a reported value of ca. 10% for fats and oils (Shon et al., 2006). The 1.9–3.1 ppm segment has been identified as proteins, peptides or amino acids (Navalon et al., 2011). The range of values for this region (54.0 – 75.2 %) are marginally higher than a reported value of ca. 50% for proteins (Shon et al., 2006), and are once again expected in wastewater (Fig. 1). The 6.0–9.0 ppm segment has been identified as aromatic compounds (Navalon et al., 2011) which have been reported as indicative of sorption behaviour (Perminova et al., 1999; Gustafsson et al., 2001; Holbrook et al., 2004), however they represent only a small fraction of the current wastewater composition (0 – 1.5 %). The middle segments contain 3.3 – 3.9 ppm which is identified as the mono- and polysaccharides region (Navalon et al., 2011). The absence of carbohydrates in the sample is unexpected since they are reported to represent ca. 40% of wastewater composition (Shon et al., 2006). Given the lack of signal in this region over three distinct sampling periods, the reason for absence of carbohydrates from this MWTP is unknown.

3.6.^{1}H NMR fractions - AHA

^{1}H NMR spectra for AHA from the current study is shown in Fig. 9(A) in comparison to two previous studies (Fig. 9B,C). Overall the spectra of all three studies

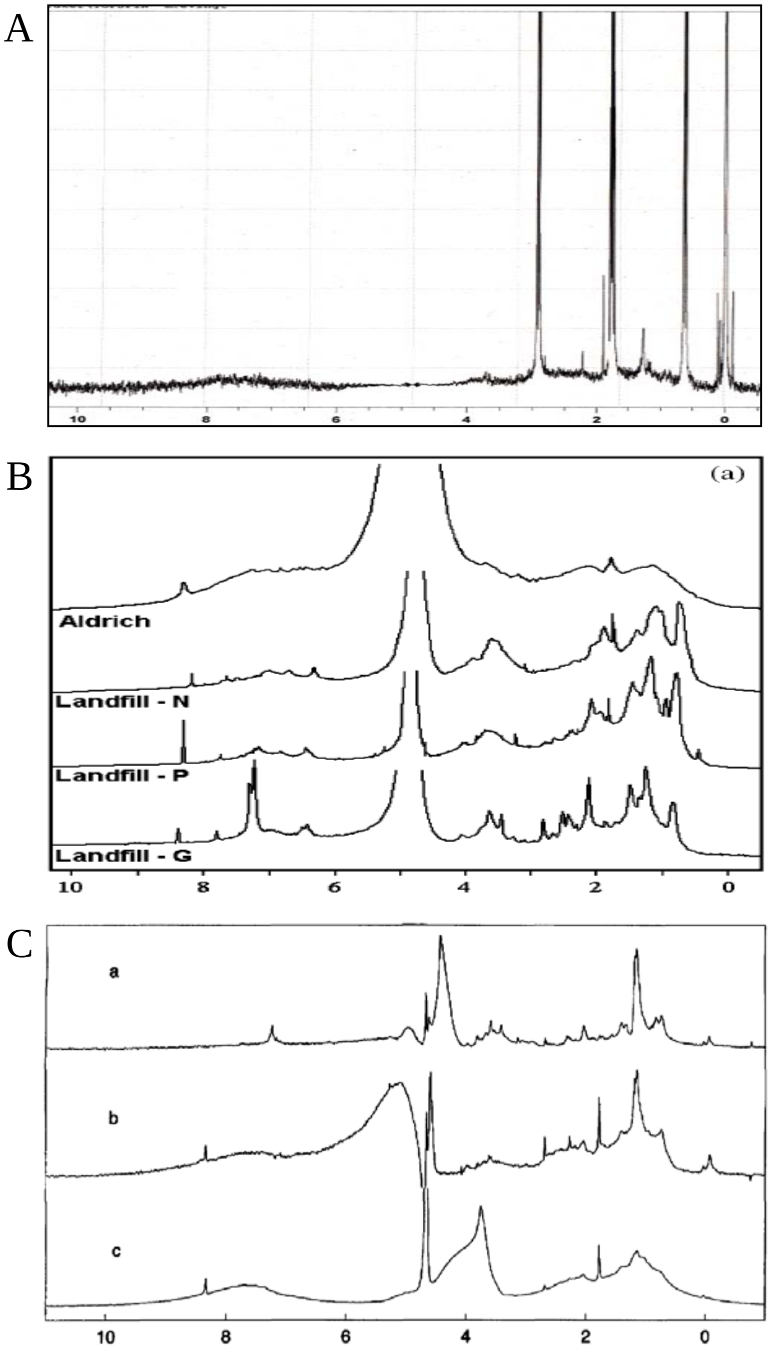

Fig. 9: ^{1}H NMR spectra of AHA. (A) current study passing 1.5 µm filter; (B) passing 0.45 µm filter various sample from Kang et al. (2002); (C) molecular weight fractionated sample after 0.45 µm filter from Hinedi et al. (1997). (a) 1000 amu, (b) 8000 amu, (c) unfractionated.

exhibit similar trends including the majority of significant peaks in the 0–3 ppm range, a broad peak in the 6–9 ppm range, and no peaks after 9 ppm. However, the spectra from Kang et al. (Fig. 9B) does not allow for much interpretation of peaks due to their broad nature and a large water peak (4.7 ppm) that has not been well processed. The spectra from Hinedi et al. (Fig. 9C) have better resolution but appear to be inconsistent in peak area and locations of a fractionated sample. For example, the 1000 amu spectrum is missing the 8.2 ppm peak and has gained a 7.2 ppm peak while the 0–2 ppm region peaks lack continuity between overlapping samples. The proportion of peak areas found within each chemical shift region for the current AHA sample is shown in Table 3. The majority of the current signal is found within the first two segments (0.5–1.9 ppm and 1.9–3.1 ppm). The 0.5–1.9 ppm segment has been identified as fatty acids, lipids or related compound and 1.9–3.1 ppm segment has been identified as proteins, peptides or amino acids (Navalon et al., 2011). The lack of peaks in the aromatic region was not expected (6.0 – 9.0 ppm) given that previous research has shown AHA to have a high aromatic content (Hinedi et al., 1997; Perminova et al., 1999; Kang et al., 2002). However, the current AHA spectrum does exhibit a broad peak in this region that may be attributed to a variety of aromatic compounds rather than individual compounds.

Aldrich humic acid (Fig. 9A) and COC (Fig. 7) spectra in the current study are quite similar overall with most of the peak area in the < 4.0 ppm region. Despite the similarities, the AHA spectrum only exhibited three major peaks as opposed to seven for COC samples. Additionally the AHA spectrum had very few smaller peaks compared with the COC samples indicating a much more homogeneous group of compounds. This result would be expected considering the diverse nature of COCs from a MWTP that is unprocessed versus the standard processed AHA sample. With further development of the NMR techniques identification of specific compounds will be invaluable in further comparisons and characterization.

4. Environmental Significance

Characterization of MWTP COC is important for the understanding of environmental loadings of both COC and HOCs, both bound and unbound, to the receiving waters. The size fractionation technique, using membrane and ultrafiltration, presented here is robust and repeatable and could be considered as a standard method for size fractionation. By considering a standard method in size characterization, researchers may more easily make comparisons between studies. Size distributions are the first step in characterization, followed by various other techniques that serve to define the COC content. UV absorbance is a simple and valuable technique, when coupled with COC concentrations, has shown to be useful in the correlation of HOC binding to COC. NMR techniques are a more direct measure of actual COC constituents rather than a surrogate measure. Given the simplicity of sample creation in the current study, any researcher without onsite access to NMR instruments can have the sample analysed by an NMR facility for a very low cost (a single sample run is 1 h for ^{1}H NMR). Further investigation of NMR results is needed for greater understanding of the technique for use in HOC – COC correlation through the MWTP process.

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CHAPTER 5

Partitioning behaviour and rate constants for binding of 1,2,4,5-tetrachlorobenzene, pentachlorobenzene, and hexachlorobenzene to primary effluent dissolved organic matter and humic acids using a gas sparging system.

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1. Introduction

Trace organic pollutants in wastewater have recently become a concern considering the potential for human health risks. Movement of pollutants both bound to organic matter (OM) and freely-dissolved, throughout the municipal wastewater treatment plant (MWTP) process is not well understood and must be further studied. Hydrophobic organic compounds (HOCs) sorption to colloids has been well studied in natural environments (Backhus et al., 1990; Chin et al., 1992; Gustafsson et al., 1997; Chin et al., 1997; Laor et al., 2002); however, few studies have investigated sorption to colloids from MWTP (Holbrook et al., 2004). Generally, aquatic colloids are defined to comprise the size fraction from 1 nm – 1 µm (Gustafsson et al., 1997) and MWTP colloids are commonly denoted as the fraction below 0.45 µm (Shon et al., 2006) (Fig. 1). The current study considers the defined colloidal range as the fraction below 1.5 µm which is the historic size fraction used for delineating colloidal and suspended solids in the MWTP process.

MWTP OM contains many constituents (Fig. 1) originating from drinking water, domestic use, water and wastewater treatment disinfection and soluble microbial products from biological treatment processes (Shon et al., 2006). Any of these constituents may have the ability to bind chemical pollutants throughout the treatment process. A more thorough evaluation of HOC – colloid sorption is especially needed for primary sedimentation effluents since colloid-associated compounds may not be removed via degradation pathways, volatilization, and/or sedimentation during secondary treatment, thereby potentially be released to natural systems via effluents into receiving water bodies and irrigation of agricultural lands (Holbrook et al., 2004).

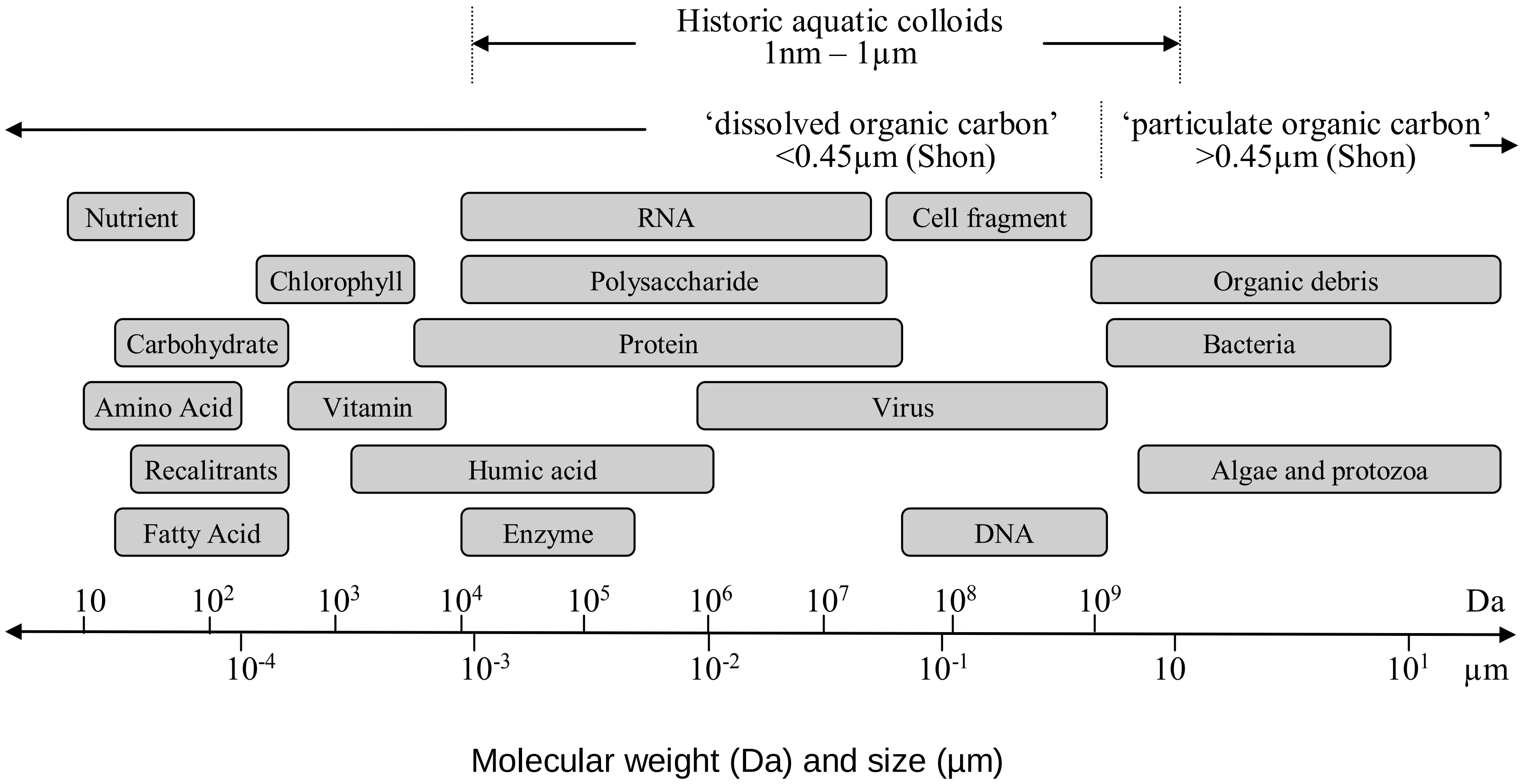


Fig. 1: Typical organic constituents in a MWTP process including size ranges and historic colloids size distinctions. Adapted from Levine et al. (1985), Lead et al. (2006), and Shon et al. (2006).

The term K_{COC} (unitless) is used to define the equilibrium partitioning relationship for a given HOC between the aqueous phase and colloidal organic carbon (COC; organic matter normalized by its carbon content). Determination of K_{COC} is important in identification of the distribution of compounds within MWTPs and in environmental compartments beyond. Methodologies for measurement of K_{COC} have been reviewed by Mott (2002) including gas-aqueous partitioning, dialysis, reverse-phase liquid chromatography, liquid-solid partitioning, fluorescence quenching, apparent solubility enhancement and solid-phase microextraction (not included in Mott 2002). Each of these methodologies have benefits and detriments, however, the current study uses the gas-aqueous partitioning approach in the determination of partitioning behaviour.

In conjunction with the K_{COC} parameter, other partitioning rates may be determined including the dissociation of chemical from COC-bound to aqueous phase (k_{12}) and the sorption from aqueous phase to bound phase (k_{21}). These rates have been determined for many other environmental compartments (Canton et al., 1977; Hiraizumi et al., 1979; Wu et al., 1986; Herman et al., 1991; Rutherford et al., 1992; Koelmans et al., 1993; Lee et al., 2002; Birdwell et al., 2007), but are lacking for MWTP research.

In this study, the sorption of three chlorobenzenes (1,2,4,5-tetrachlorobenzene, pentachlorobenzene, and hexachlorobenzene) to two organic matter sources (MWTP derived COC and Aldrich humic acids – AHA) is investigated. The chlorobenzenes are persistent organic pollutants that have been used in various industrial and agricultural processes and serve as a good model of partitioning given their similar structure, but varying hydrophobicity (as determined by octanol-water partitioning coefficient). Gas sparging has been previously used to determine gas-sparging specific Henry’s law constants (Chapter 3) which will be used to determine K_{COC} in the current study, The objectives of this study are (1) to quantify K_{COC} for the MWTP primary tank effluent; (2) to quantify K_{COC} of AHA for comparison to historic values and methodology confirmation; (3) to determine rate constants of partitioning for both effluents and AHA; and (4) to determine the potential interactions between the mix of chlorobenzenes with COC.

2. Theory

Historically, the binding of hydrophobic compounds to organic matter was considered linear over a wide concentration range (Carter and Suffet, 1982). Although research has questioned the validity of this assumption (Laor et al., 2002), over a smaller concentration range the linearity may be considered valid and can be described by:

$$K_{coc} = \frac{C_{coc}}{C_{aq}} \tag{1}$$

where C_{coc} is the bound concentration (ng m^{-3}) and C_{aq} is 'freely dissolved' (ng m^{-3}). Similarly, the air/water partition coefficient (K_{AW}; unitless) is defined as:

$$K_{AW} = \frac{C_g}{C_{aq}} \tag{2}$$

where C_g is the vapour phase concentration (ng m^{-3}). At equilibrium, with assumption of first-order kinetics a three phase (vapour, water, COC) closed system can be described by:

$$C_{coc} \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} C_{aq} \underset{k_w}{\overset{k_v}{\rightleftarrows}} C_g \tag{3}$$

where k_{12} (desorption), k_{21} (sorption), k_v (volatilization), and k_w (deposition) are first-order rate constants (d^{-1}) describing mass transfer of chemical between environmental media.

In the open environment of a gas-sparging system containing COC, water and vapour phase, an irreversible loss of compound in the system via gas stripping and volatilization will occur negating the k_{21} and k_w mass transfer rates from eq 3. Assuming the sparger has been optimized to create the condition of equilibrium between C_{aq} and C_g based on bubble/water contact time and further assuming that $k_{12} << k_v$, (Hassett and Milicic, 1985; Drouillard et al., 1998) the following expressions follow:

From eq 1 and eq 2:

$$K_{coc} = \frac{k_{21}}{k_{12}} \tag{4}$$

And the total concentration (C_T) and rate expressions follow:

$$C_T = C_{coc} + C_{aq} \tag{5}$$

$$\frac{dC_{coc}}{dt} = k_{21}C_{aq} - k_{12}C_{coc} \tag{6}$$

$$\frac{dC_{aq}}{dt} = k_{12}C_{coc} - (k_{21} + k_v)C_{aq} \tag{7}$$

$$\frac{dC_T}{dt} = -k_v C_{aq} \tag{8}$$

$$\frac{dC_g}{dt} = k_v C_{aq} \tag{9}$$

Hassett and Milicic (1985) state the following assumptions binding these equations: (i) the bound compound is non-volatile and (ii) COC does not affect k_v. Given these assumptions, the equations are solved by Hassett and Milicic (1985) using three special cases and a general case. The following cases are adaptations of the 'Initial Slope' variant used to determine Henry's law constant and k_v and the 'Steady-State' solution used for k_{12} and k_{21}.

2.1.Initial slope solution

Allowing the purge vessel to equilibrate before sparging (t = 0) and assuming $k_v >> k_{12}$, the following results from solving the initial conditions of eq 2 and 5 combined with eq 8:

$$C_T = \frac{C_T^\circ}{1+K_{coc}} e^{-k_v t} + \frac{K_{coc} C_T^\circ}{1+K_{coc}} \tag{10}$$

In a COC-free vessel, $K_{coc} = 0$, negating the second term. The resultant equation can be plotted as C_t vs. $e^{-k_v t}$ yielding the Henry's law constant volatilization rate, or first-order rate constant k_v, which can be used to determine the Henry's law constant (H) via (Drouillard et al., 1998):

$$H = k_v \frac{VRT}{F} \tag{11}$$

where V is the sparged water volume (L), R is the gas constant, T is temperature (K), and F is the gas flow rate (L h^{-1}). After determination of k_v, K_{coc} may be determined for a purge vessel containing COC using the ratio of the intercept to slope of the plot of C_T vs. $e^{-k_v t}$.

And correcting for COC concentration:

$$K_{COC} = \frac{K_{coc}}{[COC(mg/L)]} \tag{12}$$

The initial slope method is valid during the early portion of gas sparging when C_T contains C_{aq} at concentrations in equilibrium or approaching equilibrium with sorbed phases. However, as C_{aq} becomes depleted due to volatilization, the bound fraction becomes released from sorbed phases causing the slope of the line to decrease as the rate of sorbed-phase dissociation increases. Use of this region in the initial slope region will result in erroneous partitioning parameter calculations and the slope transition between the initial phase and released bound phase must be identified by careful evaluation of the curve.

2.2.Steady state solution

Under the condition where $k_{12} <<< k_v$ and when C_{aq} effectively becomes exhausted following initial gas stripping, the rate limiting step to volatilization becomes controlled by k_{12}. Although the theory recognizes COC as a single phase, it should be recognized that k_{12} and k_{21} may be multi-phase in nature owing to different size fractions and COC compositions within the sparger matrix as well as sorptive associations of the chemical with sparger walls as was demonstrated in COC-free experiments that yield non-linear behaviour (see Chapter 3). The latter artefacts would be minimized when desorption rates from HOC are slower than desorption from glass walls. Again, careful evaluation of the sparger curve is necessary to deduce transition points from mass flux being controlled by volatilization against desorption rate controlled processes.

When the mass flux of chemical loss to stripping equals k_{12}, $dC_{aq}/dt = 0$. Therefore, using eq 5, 7, and 8 results in:

$$\ln C_T = \frac{k_v k_{12}}{k_v + k_{12} + k_{21}} t + \ln C_T^{\circ} \tag{13}$$

A plot of ln C_t vs. t, the slope of the linear portion is a function of k_v, k_{12}, and k_{21}. Given k_v and K_{COC} have been determined previously via the *Initial Slope Solution*, k_{12} and k_{21} can be obtained in conjunction with the slope and eq. 4.

3. Materials and Methods

3.1. Chemicals and reagents

1,2,4,5-tetrachlorobenzene (TeCB; 98% pure), pentachlorobenzene (PeCB; 98% pure), hexachlorobenzene (HCB; 99% pure), sodium azide (NaN_3: 98% pure), 1,3,5-tribromobenzene (TBB; 98% pure) and Amberlite XAD2 (20-60 mesh) were purchased from Sigma-Aldrich (Canada). Stock solutions of 10 mg L^{-1} TBB (internal standard) and a mixture TeCB, PeCB and HCB (30, 10, and 10 mg L^{-1}, respectively) were prepared in hexane and methanol, respectively, and stored at 4 °C. Physicochemical data for the three chlorobenzenes is included in Table 1.

3.2.Wastewater sampling

Samples were taken from Little River Pollution Control Plant (LRPCP) in Windsor, Ontario, Canada. The plant serves the eastern portion of the City of Windsor and the surrounding municipalities of Tecumseh, St. Clair Beach and Sandwich South, and has two parallel and similar activated sludge-type secondary wastewater treatment systems with a combined design capacity of 60 000 m^3 d^{-1}. Five sets of samples were collected on separate days under normal dry weather conditions, spaced over 2010. On each sampling occasion, grab samples (ca. 10 L) were collected at the primary sedimentation tank using a 25 L pre-cleaned container. Samples were transported to the

Table 1: Physicochemical properties of the chemicals at 25 °C.

chemical	**MW**	**H (Pa m^3 mol^{-1})^a**	**vp (Pa)^b**	**solub. (g m^{-3})^b**	**log K_{ow} selected^b**	**log K_{ow} range^c**
TeCB	215.9	56.5	9.86	1.27	4.5	4.46 – 5.05
PeCB	250.3	33.3	0.88	0.65	5	4.88 – 5.79
HCB	284.8	29.9	0.245	0.005	5.5	4.13 – 6.53

[a]Chapter 3, [b]Suntio et al., 1988; [c]References found within Suntio et al.

laboratory within one hour of collection and treated with ca. 100 mg L^{-1} sodium azide to inhibit microbial degradation. Samples were filtered through 1.5 µm precombusted glass fibre filters (Whatman 934AH). Aliquots of the filtrate were used for further size fractionation and various other analysis including total and volatile suspended solids (TSS and VSS, respectively) as per “Standard Methods” (APHA, 1998).

3.3.Humic acid solution preparation

Humic acid sodium salt (Sigma Aldrich) (ca. 2 g L^{-1}) was dissolved in MilliQ water, stirred using a Teflon stir bar for 1 h and filtered using a 1.5 µm glass fibre filter (Whatman 934AH). A stock buffer solution was prepared by dissolving 3.4 g of KH_2PO_4 and 3.5 g of K_2HPO_4 in 1 L of MilliQ water. The humic acid solution was buffered to a pH of 6.7 and 100 mg of sodium azide was added to prevent degradation. The final COC solution was 198.6 mg L^{-1} as determined by a Shimadzu TOC-5000 analyzer. The solution was diluted using MilliQ to approximate primary effluent COC concentrations for use in experiments.

3.4.Multi-sparger system

A multi-sparger system design and method was used for all experiments as described previously in Chapter 3. Duplicate or triplicate 1 L samples of three treatments included: MilliQ water, 1.5 µm effluent sample, and humic acids. Samples were spiked with 100 µL of the chlorobenzene mixture (600, 200, 200 pg μL^{-1} of TeCB, PeCB, and HCB, respectively), mixed through shaking, sealed with polyfilm, and allowed to equilibrate ca. 18-24 h in a water bath prior to commencing experiments. XAD2 resin traps were spiked with TBB prior to experimental use as an internal standard to verify extraction efficiency. For further methods please refer to Chapters 3 and 4.

3.5.Analytical methods

Analysis of all samples was carried out on a Varian 3600 GC equipped with split/splitless injector, a 30 m X 0.32 mm fused silica DB-5 column with a 0.25 μm film thickness (J&W Scientific) and an ECD detector. The injector was maintained at 250 °C with a flow rate of 2 mL min^{-1} He. A 1 μL injection was made into a 253 μm liner and the column was held at 140 °C for 2 min. Subsequently, the column was raised to 192 °C at 6.5 °C min^{-1} ramp. The makeup flow rate was 29 mL min^{-1} N_2 and detector temperature at 250 °C. The limit of detection (LOD) is defined as the minimum amount of analyte which produces a peak with a signal-to-nose ratio equal to 3. A PeCB standard was injected prior to and post all experimental runs as quality control and expected to fall within a standard deviation of standard curve values. XAD2 resin traps spiked with TBB prior to experimental use as internal standards had recoveries from 94 – 106%.

4. Results and Discussion

4.1.Aldrich humic acid partitioning

Table 2 shows results of AHA sparging experiments. TeCB $\log K_{AHA}$ average (4.10) and range (3.92 – 4.31) are higher than $\log K_{COC}$ values of the current study (Table 3), but are similar to the 1,2,3,5-tetraCB isomer. PeCB $\log K_{AHA}$ average (4.57) and range (4.40 – 4.79) are higher than the current study $\log K_{COC}$ values (Table 3), but are within the range of literature values (Table 2). HCB logK_{COC} average (4.70) and range (4.51 – 4.91) are markedly higher than logK_{COC} values within this study (Table 3), however, are similar to literature values (Table 2). AHAs have been used extensively in the literature as a 'surrogate' of naturally occurring organics in the environment, since it is commercially available and pre-processed. AHAs are interesting to use as a validation of experimental methods, as well as for a consistent source for comparison to various other organics in the MWTP process. Use of commercial humic acids as representative of NOM has been criticized and any correlation to actual MWTP COC should be closely evaluated (Perdue et al., 1982; Malcolm et al., 1986; Raber et al., 1998; Niederer et al., 2007).

4.2.Theoretical validation

The two assumptions made by Hassett and Milicic (1985) for the gas sparging technique must be validated prior to generating experimental data. The first assumption is the sparging gas must reach equilibrium with the water phase before exiting the water column. This column height equilibration assumption has been studied extensively (Mackay et al., 1979; Matter-Mueller et al., 1981; Yin and Hassett, 1986; Dunnivant et al., 1988; ten Hulscher et al., 1992; Drouillard et al., 1998). For the chlorobenzenes in the current study, a 40 cm water column was previously determined to allow for equilibrium (ten Hulscher et al., 1992); therefore, the current 60 cm water column height is considered acceptable for equilibrium and compares well with a recent 62 cm water column used by Jantunen and Bidleman (2006) for a similar study.

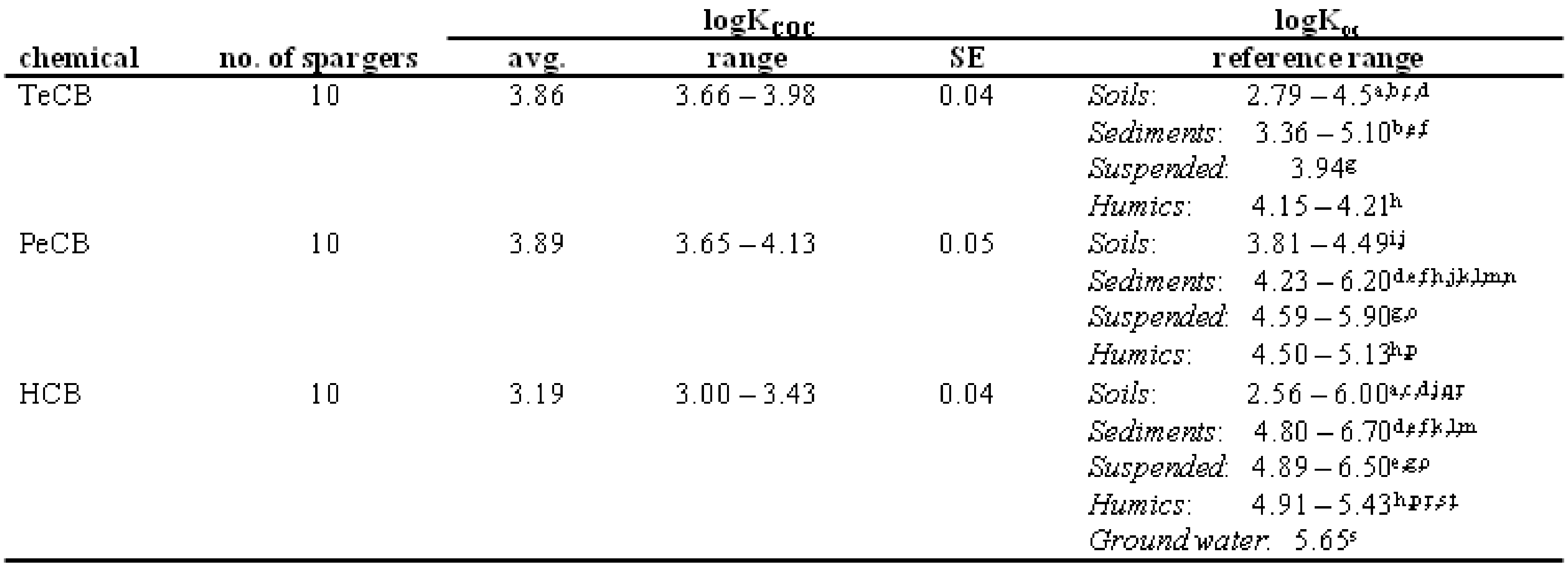
Prior to testing the second assumption, a representative set of depletion curves using a single TeCB experimental set of control and treatment spargers was plotted (Fig.

Table 2: Summary of K_{COC} values for Aldrich humic acid sample calculated using initial slope method from gas sparging results and comparison literature values.

		$\log K_{COC}$			
chemical	**no. of spargers**	**avg.**	**range**	**SE**	**reference range**
TeCB	4	4.10	3.92 – 4.31	0.06	4.15 – 4.21[a]
PeCB	4	4.57	4.40 – 4.79	0.05	4.50 – 5.13[a,b]
HCB	4	4.70	4.51 – 4.91	0.07	4.91 – 5.43[a,b,c,d,e]

[a] Resendes et al., 1992; [b] Urrestarazu Ramos et al., 1998; [c] Enfield et al., 1989; [d] Freidig et al., 1998; [e] Yabuta et al., 2004

Table 3: Summary of K_{COC} values for 1.5µm primary samples calculated using initial slope method from gas sparging results and comparison literature values.



		$\log K_{COC}$			$\log K_{oc}$
chemical	**no. of spargers**	**avg.**	**range**	**SE**	**reference range**
TeCB	10	3.86	3.66 – 3.98	0.04	*Soils*: 2.79 – 4.5^{a,b,c,d}
					Sediments: 3.36 – 5.10^{b,e,f}
					Suspended: 3.94^{g}
					Humics: 4.15 – 4.21^{h}
PeCB	10	3.89	3.65 – 4.13	0.05	*Soils*: 3.81 – 4.49^{i,j}
					Sediments: 4.23 – 6.20^{d,e,f,h,j,k,l,m,n}
					Suspended: 4.59 – 5.90^{g,o}
					Humics: 4.50 – 5.13^{h,p}
HCB	10	3.19	3.00 – 3.43	0.04	*Soils*: 2.56 – 6.00^{a,c,d,j,q,r}
					Sediments: 4.80 – 6.70^{d,e,f,k,l,m}
					Suspended: 4.89 – 6.50^{e,g,p}
					Humics: 4.91 – 5.43^{h,p,r,s,t}
					Ground water: 5.65^{s}

[a] Briggs, 1981; [b] Schwarzenbach et al., 1981; [c] Walton et al., 1992; [d] Delle Site, 2001; [e] Oliver and Charlton, 1984; [f] Djohan, et al., 2005; [g] Masunaga, 1996; [h] Resendes et al., 1992; [i] Paya-Perez et al., 1991; [j] Wu and Gschwend, 1986; [k] Karickhoff and Morris, 1985; [l] Oliver, 1987a; [m] Schrap et al., 1994; [n] Cornelissen et al., 1997; [o] Oliver, 1987b; [p] Urrestarazu Ramos et al., 1998; [q] Rippen et al., 1982; [r] Enfield et al., 1989; [s] Freidig et al., 1998; [t] Yabuta et al., 2004.

2). All experiments and chemicals exhibited similar trends. As found previously in Chapter 3, the control spargers exhibited three distinct regions, an initial slope phase (< 6 h), transitional phase (6 ~ 12 h), and steady-state phase (> 12 h) (Fig. 2). Treatment spargers also showed a similar trend, albeit with lower overall cumulative masses indicative of chemical being sorbed onto organic matter in the current study. Given the similarity with the previous study (Chapter 3) where the volatilization rate was found not to be constant, it is expected that the current rate will also be variable. To test the assumption of a constant k_v a plot of the natural logarithm form of eq 11 for control spargers without COC was made (Fig. 3). As is clearly indicated by Fig. 3, the volatilization rate exhibits three distinct regions, invalidating the second assumption of a constant k_v. Analysis of covariance (ANCOVA) was used to determine if the slopes differed between the three regions. Despite graphical differences in the plots and marked differences in slopes and intercepts, especially between initial and steady-state phases, no statistical differences between slopes were found ($p > 0.05$). Unfortunately, the strength of the statistical analysis was low due to only three points being available for analysis in the current study. Previously, the Chapter 3 study was shown to be able to discern statistical differences due to the extensive set of data points available. Of note for the current study, if the regression lines for the steady-state region are used to determine a 48 h data point, the ANCOVA results in statistically different initial and steady-state regions.

Despite a lack of statistical corroboration, it is apparent that the second assumption of constant k_v is invalid over long sparging durations. This result has been previously attributed to partitioning to glass surfaces within the sparger. Despite the lack

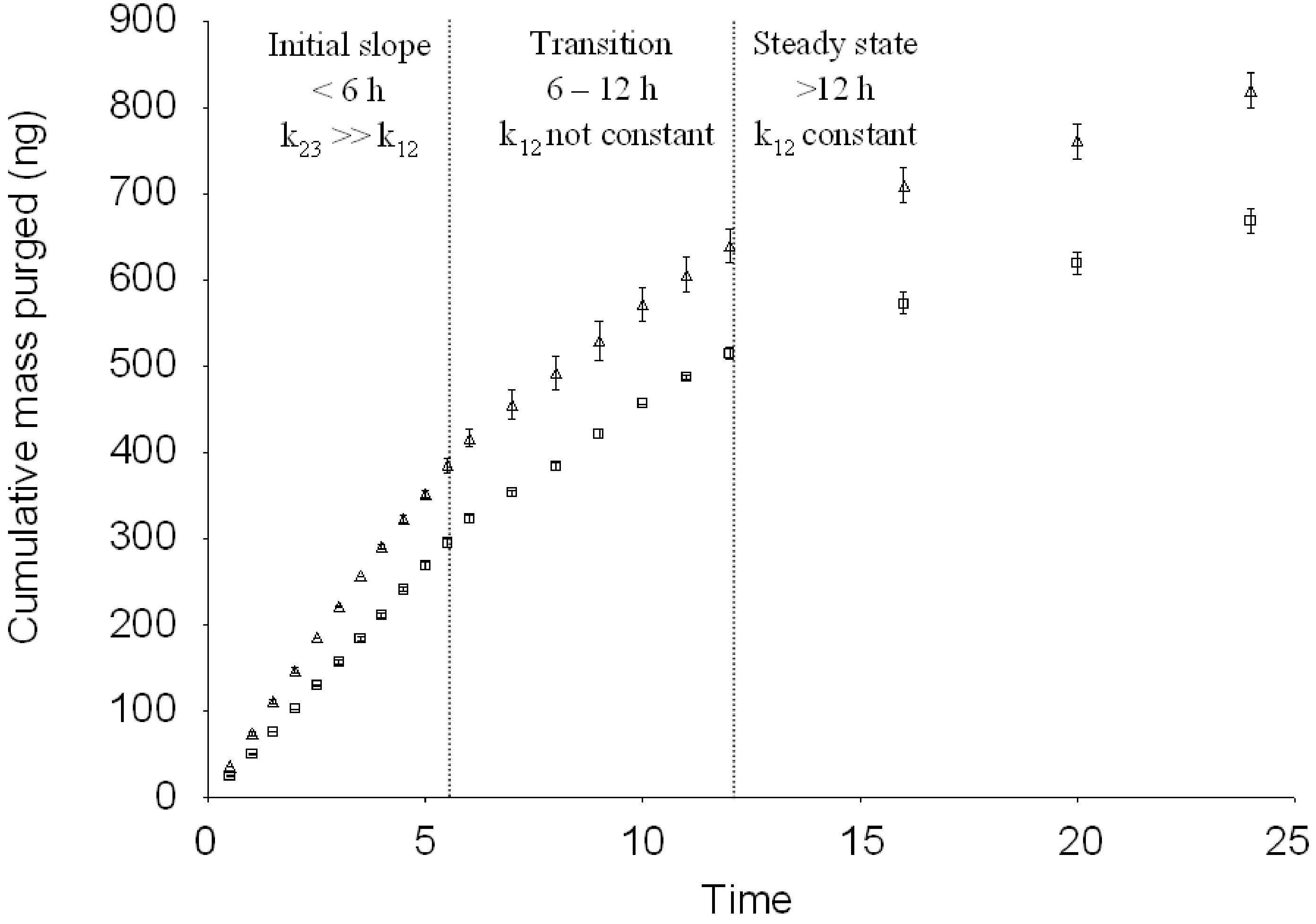


Fig. 2: Depletion curves for a representative experimental run and chemical (TeCB). Triangles represent control spargers (MilliQ) and squares represent 1.5 µm spargers.

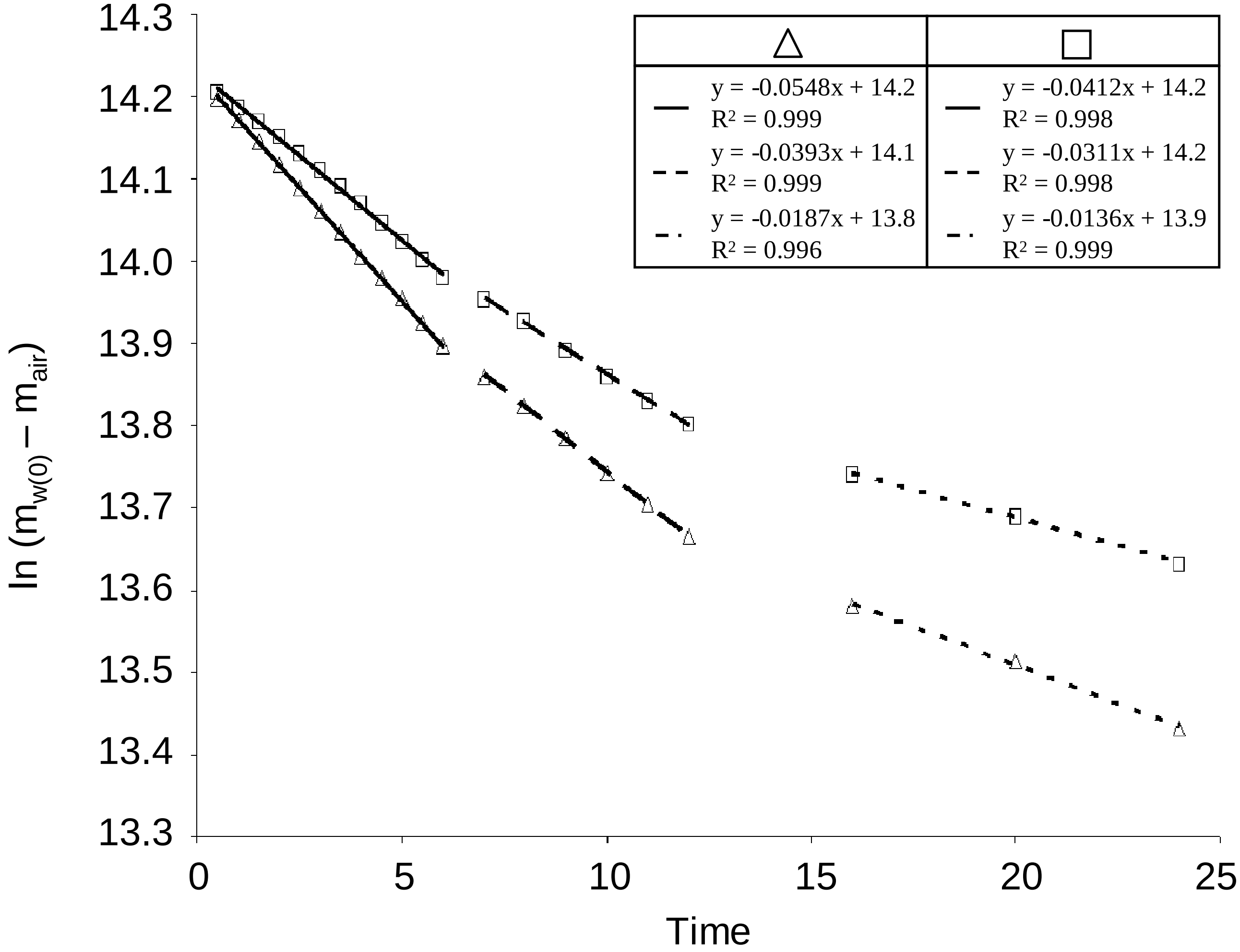


Fig. 3: Least squares linear regression of the natural logarithm of initial (spiked) minus measured cumulative mass (trapped) over time. Slope of initial regression line (see text for further detail) is the first-order volatilization rate constant (k_v). Triangles represent control spargers (MilliQ) and squares represent 1.5 µm spargers.

of constant k_v throughout sparging, the method of using the initial slope phase to determine partitioning parameters is valid considering k_v is constant in this region and is much greater than the desorption rate k_{12}.

4.3.Primary effluent partitioning – Initial slope method

A representative C^t vs. $e^{-k_v t}$ graph for TeCB is shown in Fig. 4, which was used to determine K_{COC} using eq 11 via the slope and intercept. Henry's law values derived from k_v for spargers were determined previously (Table 1), 12 XAD2 samples were used over a 6 h interval to determine partitioning behaviour, resulting in excellent linearity over the initial slope range for all experiments (10 total spargers over 5 experiments). Values for calculated $\log K_{COC}$ and reference $\log K_{oc}$ ranges (for various organics) are shown in Table 2. Overall reproducibility was very good for each compound (TeCB, PeCB, and HCB) in the current study.

TeCB $\log K_{COC}$ average (3.86) and range (3.66 – 3.98) both are within reference ranges for soils (2.79 – 4.5) and sediments (3.36 – 5.10), as well as being very similar to a suspended particulates measurement (3.94) (Table 3). The current isomer AHA $\log K_{oc}$ values are unavailable, however, in comparison with reported 1,2,3,5-tetraCB values (Resendes et al., 1992) the current $\log K_{COC}$ average and range both fall below literature AHA $\log K_{oc}$ values. PeCB $\log K_{COC}$ average (3.89) and range (3.65 – 4.13) are in reasonable agreement with soil $\log K_{oc}$ range (3.81 – 4.49). Reference $\log K_{oc}$ ranges for sediments, suspended particulates, and AHA are all markedly higher than the current study's average and ranges (Table 3). HCB $\log K_{COC}$ average (3.19) and range (3.00 – 3.43) fall within the wide $\log K_{oc}$ of soil references (2.56 – 6.00). Reference $\log K_{oc}$ ranges

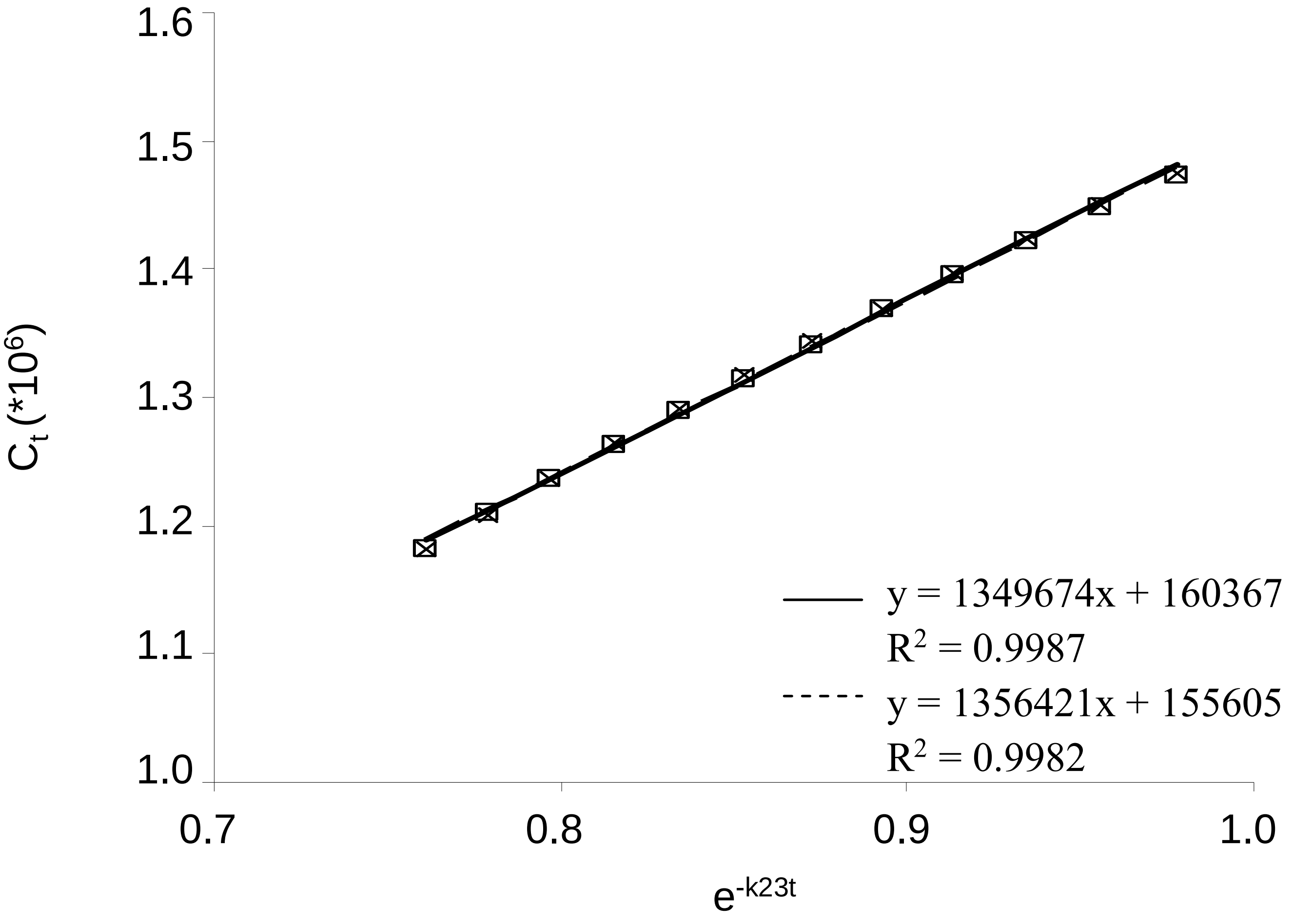


Fig. 4: Least squares linear regression of the total concentration versus exponential slope of control spargers over time for treatment spargers over the initial slope period (TeCB).

Given the availability of well documented partitioning to organics in natural environments (Table 3) and the lack of partitioning research in MWTPs, the current compounds' $\log K_{COC}$ may only be compared in a relative nature. Additionally, given the vast differences in organic sources, reference ranges of $\log K_{oc}$ values are quite large even within each category presented (Table 3), as well as in natural water systems for other hydrophobic compounds (Gustafsson et al., 2001). Gustafsson and Gschwend (1997) have found that partitioning of pyrene to the colloidal fraction of seawater is lower than that of literature values for sediments and soils. These differences may be attributed to variability in size, aromaticity, and polarity (Gustafsson et al., 2001). Translating these differences into the current MWTP COC, it would be expected that $\log K_{COC}$ values would be lower than $\log K_{oc}$ of soils and sediments.

Based on $\log K_{ow}$ values of 4.5, 5, 5.5 for TeCB, PeCB, and HCB (Table 1), it would be expected that $\log K_{COC}$ values would increase with higher hydrophobicity, thus TeCB < PeCB < HCB. However, the current $\log K_{COC}$ values do not follow the expected pattern, with TeCB ~ PeCB > HCB. HOC sorption mechanisms to COC may include molecular interactions including van der Waals dispersive, dipole-induced-dipole, dipole-dipole, and hydrogen bonding (Schwarzenbach et al., 2003). These sorption mechanisms may result in adsorption (surface phenomenon) or absorption (hydrophobic exclusion from water) partitioning behaviour. Given the behaviour of chlorobenzenes reported in the literature (Table 3) (adhering to hydrophobicity partitioning expectations), mechanisms by which the current unexpected sorption to COC occur must be determined.

Given the close similarity between the current chlorobenzenes, only vary by degree of chlorination, differences in partitioning due to electronegativity are unlikely.

Additionally, due to the rigid structure of a single benzene ring, changes in structural formation leading to varying partitioning are unlikely to occur. Structural conformations have shown to be important in the partitioning behaviour of PCBs (Kukkonen et al., 1990), with numerous isomers exhibiting varying degrees of partitioning.

Potential variables that may affect partitioning behaviour may include molecular mass, compound competition, and COC characteristics. Molecular masses of the chlorobenzenes are 216 Da (TeCB), 250 Da (PeCB) and 285 Da (HCB). For partitioning to occur, the COC must be at least of similar mass and size as the partitioning chemical (Gustafsson et al., 2001). Therefore, it may be deduced that TeCB would bind to a smaller size COC particle versus PeCB and HCB. The current study COC fraction below 1 kDa was a majority of the COC (67% of total mass). In a recent study, Holbrook et al. (2004) found a similar trend of smaller size fractions for STP final effluents. Given the large proportion of the small size fraction, with unknown actual sizes, the reduced potential for higher mass PeCB and HCB molecules to partition to smaller COC size fractions may result in their lower than expected $\log K_{COC}$ values compared to literature sources (Table 3).

Competition for sorption sites between the chlorobenzenes may be occurring, with preferential binding of the smaller TeCB molecules. Pan et al. (2007) have recently questioned the use of single-solute sorption experiments due to the unrealistic interactions that may occur in comparison to real-world polluted samples. In their study, phenanthrene and pyrene showed distinct competition for sorption sites of AHA and peat humic acids at similar organic concentrations as in the current study (40 mg OC mL^{-1}).

However, chemical concentrations were much higher than in the current study and the smaller size fractions were discarded (< 3 500 kDa) (Pan et al., 2007).

A comparison of wastewater COC partitioning behaviour to natural organic matter may be erroneous. Since the OC is generated from different sources, it may differ in size, structure and functionality, thereby exhibiting variable partitioning behaviour than that predicted by physicochemical properties (Ma et al., 2001; Drewes et al., 2002; Holbrook et al., 2004). For example, the large contribution of the smaller size fraction to the overall COC mass is in contrast to other organic matter sources which typically have greater mass contributions from larger fractions (Perret et al., 1994). Another example is the variation of humic acid, fulvic acid, and hydrophilic fractions between wastewater and river waters (Ma et al., 2001); such variation would impact partitioning behaviour.

4.4.Rate constants - steady state

A representative ln C_T vs. t graph is shown for TeCB indicated by the dotted line (Fig. 3). All spargers exhibited excellent linearity over the steady-state region ($R^2 > 0.98$). Equations 4 and 21 were used in conjunction with the slope of Fig. 4 to determine rate constants. Rate constants, both desorption (k_{12}) and sorption (k_{21}) are shown adjusted to current COC concentrations (L mg^{-1} h^{-1}) in Table 4. To our knowledge, this is the first study to determine rate constant data for a MWTP primary sedimentation tank. Desorption rates have been determined for many hydrophobic chemicals for sediments (reviewed in Birdwell et al., 2007), soils (Wu et al., 1986; Rutherford et al., 1992; Lee et al., 2002), phytoplankton (Canton et al., 1977; Herman et al., 1991; Koelmans et al. 1993) and zooplankton (Hiraizumi et al., 1979). The current k_{12} range is in the order of magnitude of previous studies, which are uncorrected for COC concentration under the assumption that the rate is unaffected by solids concentration (Fig. 5). Figure 5 shows data from soil and sediment studies found in literature in a log k_{12} versus log K_{oc} plot, which has shown to exhibit a linear inverse relationship (Brusseau et al., 1990; Karickhoff et al., 1985). All data points for AHA and 1.5 µm data in the current study fit well within the literature data; after addition to previous data the linear regression improved ($r^2 = 0.909$ for Koelmans et al. 1993, $r^2 = 0.934$ currently). Phytoplankton data did not fit the linear model (Koelmans et al., 1993). Despite the increased correlation, there was a marked difference in AHA and 1.5 µm data. AHA data are biased towards faster desorption for a given K_p. Since AHA are the only non-natural organics presented in the data, the partitioning behaviour may vary markedly with naturally occurring organics that have not been extensively processed and modified. Removal of AHA data improves the linear correlation markedly ($r^2 = 0.956$). The 1.5 µm data for the three chlorobenzenes fall within the literature data, however, when considered independently, appear to not be linearly correlated. However, upon inspection of the literature data, this trend appears to occur frequently and may be due to the inherent uncertainty of the k_{12} determination.

Sorption data (k_{21}) are found as a result of eq 4. This sorption constant is markedly faster than the calculated desorption constant (k_{12}) (Table 4) and results from an 18 – 24 h incubation period in which sorption occurs. Hydrophobic organic compounds, such as HCB, have been shown to attain equilibrium over a very short period of

Table 4: Summary of k_{12} (bond to aqueous) and k_{21} (aqueous to bond) rate constants for 1.5 µm and HA samples calculated using steady state slope method from gas sparging.

chemical	no.	k_{12} (h^{-1})*10^4 avg.	SE	range	$t_{1/2}$ (d)	k_{21} (h^{-1}) avg.	SE	range	$t_{1/2}$ (min)
1.5 µm									
TeCB	6	7.70	2.04	3.35 – 17.3	37.5	5.38	1.61	2.72 – 13.2	7.7
PeCB	6	3.07	0.34	2.00 – 4.51	94.1	2.25	0.40	1.18 – 3.94	18.8
HCB	6	3.81	0.74	1.54 – 5.81	75.8	0.65	0.20	0.16 – 1.56	63.9
HA									
TeCB	2	8.77	0.83	7.32 – 10.2	32.9	15.7	0.38	15.1 – 16.4	2.6
PeCB	2	1.81	0.14	1.56 – 2.05	159.5	5.01	0.62	3.93 – 6.09	8.3
HCB	2	2.73	0.06	2.63 – 2.83	105.8	8.84	0.17	8.56 – 9.14	4.7

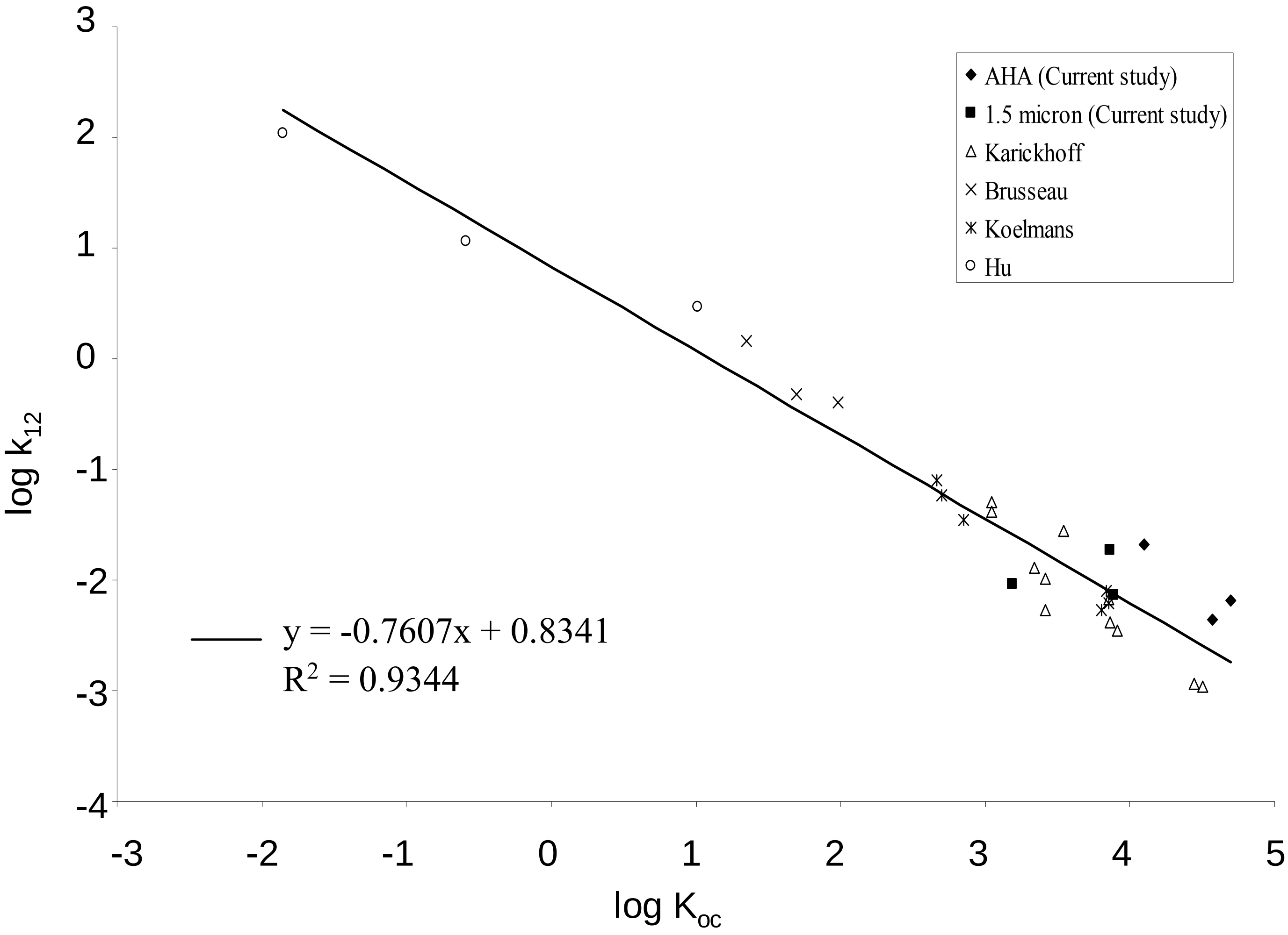


Fig. 5: Chlorobenzene log k_2 versus log K_{oc} for current study AHA and 1.5 μm data and various other studies. Regression line includes only literature data (unfilled symbols).

time (minutes to hours) (Yabuta et al., 2004; Poerschmann et al., 1997; Backhus et al., 1990; Schlautman et al., 1994). In the current study calculated sorption half-lives ($t_{1/2}$) were 7.7, 18.8, and 63.9 min for TeCB, PeCB and HCB 1.5 µm treatments (Table 4). In comparison, AHA half-lifes were all markedly faster with each being less than 10 min (Table 4). For both AHA and 1.5 µm treatments, steady-state equilibrium was easily attained overnight. In contrast to the current study, sediment equilibration duration may be considered for a much longer term (days to months) considering potential for a slower absorption in this media and the potential for longer term equilibrium. Given the residence time of wastewater COC, increasing sorption times for a MWTP sample would be unadvisable.

5. Environmental Significance

HOC removal from MWTP effluents is dependent on sorption to solids, biodegradation by biomass, and volatilization. An important mechanism of HOC transport throughout the process is via COC, which does not settle and renders HOCs inaccessible for microbial degradation and volatilization. Only the so-called freely-dissolved fraction (unbound to COC) is available for these processes. The primary effluent has reduced organics compared with influent primary, however, it has a much greater proportion of the COC fraction. Through a determination of the partitioning behaviour, including $\log K_{COC}$, k_{12}, and k_{21}, the sorption behaviour of three chlorobenzenes was determined. Results may be used to investigate sorption of other chemicals of concern and to better represent partitioning behaviour in MWTP studies. Sorption of the chlorobenzenes was novel in comparison to other organic media, requiring further study and expansion of knowledge beyond typical physicochemical property correlations. As noted extensively in the literature, AHAs are not a comparable material to COC and cannot be used to reasonably determine partitioning. Despite this caveat, AHAs are an excellent synthetic organic matter that may be used for validation of experimental methods. Having this validation will add strength in the comparison of natural organic material between various studies and sources.

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CHAPTER 6

Sorption behaviour of 1,2,4,5-tetrachlorobenzene, pentachlorobenzene, and hexachlorobenzene to cross-flow ultrafiltration fractionated 1 kDa primary sewage effluents.

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1. Introduction

Many domestic and commercial chemicals, including hydrophobic organic chemicals (HOCs), are partially removed during municipal wastewater treatment plant (MWTP) processes. Several HOCs may decrease in concentration to a level that is non-toxic to the surrounding environments. However, the fate of these HOCs is highly dependent on their sorption behaviour to dissolved organic carbon (DOC) throughout the system. Sorption of HOCs depends on physicochemical properties of both sorbate (ie. hydrophobicity) and sorbent (ie. structure) (Karickhoff, 1985; Chin et al., 1992; Rutherford et al., 1992; Schlautman et al., 1993; Perminova et al., 1999; Gustafsson et al., 2001; Poerschmann et al., 2001).

Of major importance in the MWTP process is DOC in the form of colloidal organic carbon (COC). Colloids are ubiquitous in the environment and can be defined as nanoparticles, macromolecules, or assemblages between 1 nm and 1 µm in size (Fig. 1; Lead et al., 2006). Colloids can be functionally described as particles "immune to gravity" (Graham, 1861) and having the ability to bind other compounds; therefore, assignment to specific size fractions may not fully encompass the entire colloid fraction. In sewage wastewater, historically a 1.5 µm filter has been used to delineate total suspended solids (greater than 1.5 µm) and total dissolved solids (passing 1.5 µm). Given the use of this filter fraction in many standard methods, we conclude that it is a reasonable differentiation between particulate and colloidal organic matter during the wastewater treatment process. However, the lower cut-off for the colloid (able to bind chemical) and truly-dissolved (unable to bind chemical) is debatable. Currently a range of 500 – 1000 Da has been considered a cut-off below which sorption is negligible

(Gustafsson et al., 2001; Backhus et al., 1990; Backhus et al., 2003; Holbrook et al., 2004). However this range may only be a limit of current size fractionation methods (eg. ultrafiltration) rather than a truly ‘chemcentric’ limit thereby needing further study (Gustafsson et al., 1997). In the current study, the colloidal fraction is considered to be passing 1.5 µm filters with the inclusion of the so-called ‘truly-dissolved’ fractions.

A limitation to the determination of the so-called ‘truly-dissolved’ fractions historically has been the lack of methods to separate COC into size fractions. Physical separation using filtration techniques started with gravimetric filter papers, improved with the introduction of stirred-cell ultrafiltration, and have recently been enhanced using tangential or cross-flow ultrafiltration (Gustafsson et al., 1997). The ultrafiltration technique has become widely used in isolation of both environmental (Wilding et al., 2004; Liu et al., 2005; Zhou et al., 2007; Maskaoui et al., 2007; Kottelat et al., 2008; Maskaoui et al., 2010) and MWTP colloids (Holbrook et al., 2004; Worms et al., 2010). The 1 kDa COC limit has been qualified as reasonable based on the size of HOCs in relation to colloid sizes, indicating that only COC of a specific size is able to truly act as a sorbent (Gustafsson et al., 1997). However, small HOC chemicals, such as those within the current study including 1,2,4,5-tetrachlorobenzene, pentachlorobenzene, and hexachlorobenzene are markedly smaller than PAHs considered in other studies, leading to the assumption that the true lower limit for some HOCs lies below the 1 kDa limit.

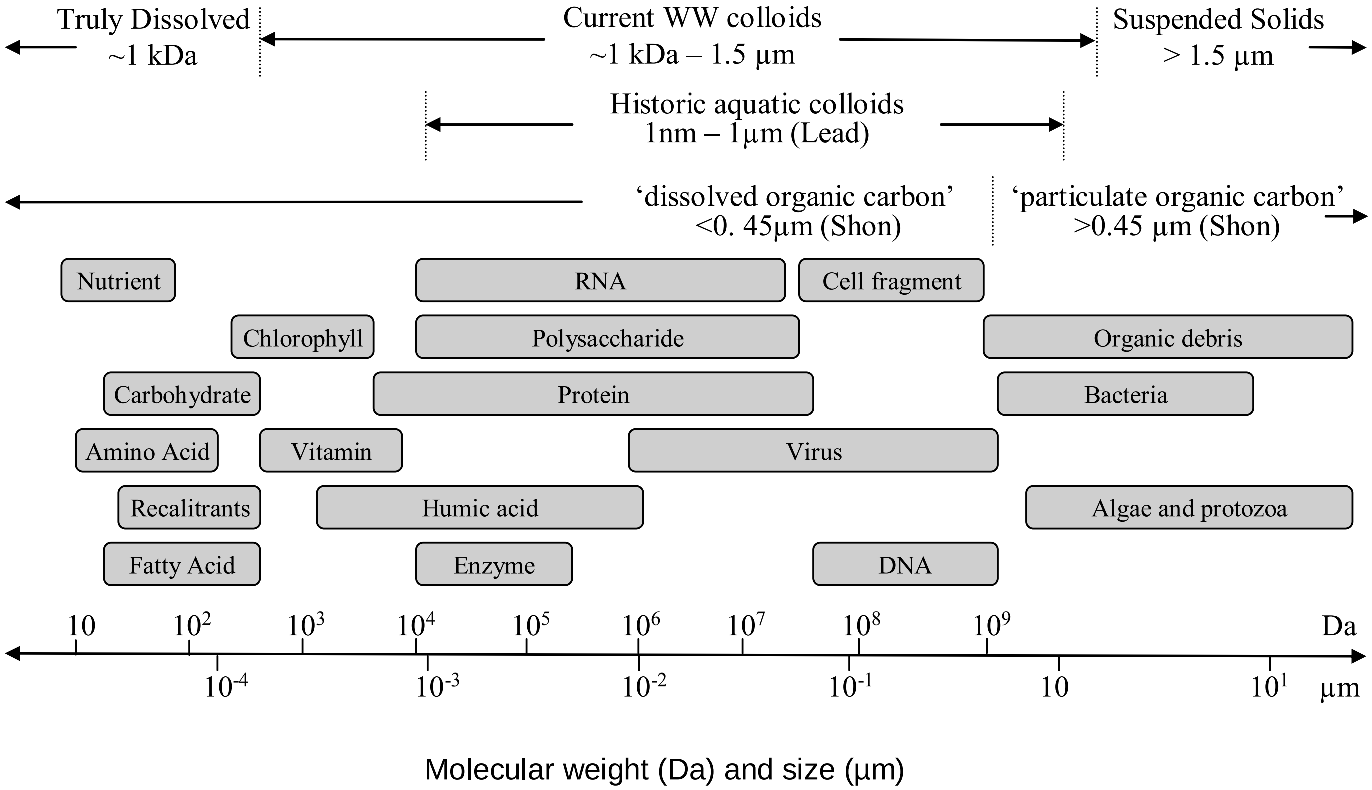

Fig. 1: Typical organic constituents in a MWTP process including size ranges and historic and current organic matter size distinctions. Adapted from Levine et al. (1985), Lead et al. (2006), and Shon et al. (2006).

The objective of the current study is to determine if the 1 kDa limit to COC partitioning is valid. Using the gas sparging technique, and various size fractions of organics for comparison, spiked chlorobenzene partitioning was investigated using the primary effluent derived from a MWTP. The primary effluent was chosen since HOCs partitioned to COC are not readily accessible for volatilization and degradation in the secondary MWTP treatment and may be carried to receiving environments through final MWTP effluents.

2. Theory

The description of the gas sparging method is shown elsewhere (Chapter 5); the following is a brief overview relevant to the current study and the calculation of the partitioning coefficient, K_{COC}. After spiking, the purge vessel is equilibrated before starting the sparging (t = 0). The first assumption is that the rate of volatilization initially is much greater than the dissociation rate, the following equation results from first principles (eq 13: Chapter 5):

$$C_T = \frac{C_T^{\circ}}{1+K_{coc}} e^{-k_v t} + \frac{K_{doc} C_T^{\circ}}{1+K_{coc}} \tag{1}$$

where C_T is the total concentration, C^o_T is the initial concentration, and k_v is the first-order volatilization rate. In a COC-free vessel, $K_{COC} = 0$, eq 1 reduces to:

$$C_T = C_T^{\circ} e^{-k_v t} \tag{2}$$

Therefore, a plot of C_t vs. $e^{-k_v t}$ (or as the natural logarithm shown in Fig. 2) in COC-free water will yield the Henry's law constant (H) calculated via:

$$H = k_v \frac{VRT}{F} \tag{3}$$

where V is the sparged water volume (L), R is the gas constant, T is temperature (K), F is the gas flow rate (L h^{-1}). The H value is determined independently for each sparging experiment, however, the average value is shown in Table 1. After determination of k_v, K_{coc} may be determined for a purge vessel containing COC using the ratio of the intercept to slope of the plot of C_T vs. $e^{-k_v t}$ by the following equations (in conjunction with eq. 1 above):

$$m = \frac{C_T^\circ}{1 + K_{coc}} \tag{4}$$

$$b = \frac{K_{coc} C_T^\circ}{1 + K_{coc}} \tag{5}$$

Solving eqs 4 and 5:

$$K_{coc} = \frac{b}{m} \tag{6}$$

And correcting for COC concentration:

$$K_{COC} = \frac{K_{coc}}{[COC(mg/L)]} \tag{7}$$

where K_{COC} is the corrected partitioning coefficient and COC (mg/L) is the dissolved organic carbon concentration within the sparger. During the initial phase of volatilization, the stripping process should be linear until freely dissolved chemical becomes depleted. Subsequently, the slope is expected to decrease as volatilization becomes rate limited by the chemical dissociation rate.

3. Materials and Methods

3.1. Chemicals and reagents

1,2,4,5-tetrachlorobenzene (TeCB; 98% pure), pentachlorobenzene (PeCB; 98% pure), hexachlorobenzene (HCB; 99% pure), sodium azide (NaN_3: 98% pure), 1,3,5-tribromobenzene (TBB; 98% pure) and Amberlite XAD2 (20-60 mesh) were purchased from Sigma-Aldrich (Canada). Stock solutions of TBB (internal standard) and a mixture TeCB, PeCB and HCB were prepared in hexane and methanol, respectively, and stored at 4 °C. Solid NaN_3 was added to all sewage samples (ca. 100 mg L^{-1}) to prevent degradation. Physicochemical parameters of the chlorobenzenes are shown in Table 1.

3.2. Wastewater sampling

Samples were taken from Little River pollution control plant (LRPCP) in Windsor, Ontario, Canada. The plant serves the eastern portion of the City of Windsor and the surrounding municipalities of Tecumseh, St. Clair Beach and Sandwich South, and has two parallel and similar activated sludge-type secondary wastewater treatment systems with a combined design capacity of 60 000 m^3 d^{-1}. Approximately 10 L grab samples were collected at the primary sedimentation tank using a 25 L pre-cleaned container during June and December, 2010 under normal dry weather conditions. Samples were transported to the laboratory within one hour of collection and treated with ca. 100 mg L^{-1} sodium azide to inhibit microbial degradation.

Table 1: Physicochemical properties of the chemicals at 25 °C.

chemical	MW	CAS#	structure	V_p(Pa)[a]	solub.(g/m^3)[a]	S_M[b]	log K_{ow}[a]	H[c] (atm*m^3/mol)*10^4
TeCB	215.9	95-94-3	$C_6H_2Cl_4$	9.86	1.27	175.2	4.5	5.29
PeCB	250.3	608-93-5	C_6HCl_5	0.88	0.65	192.3	5	3.18
HCB	284.8	118-74-1	C_6Cl_6	0.245	0.005	209.4	5.5	2.87

[a] Suntio et al.; [b] Surface area (S_M) in angstroms: Sabljic, A. 1987; [c] McPhedran et al., 2011.

3.3.Filtration

The sample was filtered through a series of gravimetric filters in the following order: 1.5 µm glass fiber filters (Whatman 934AH); 1.1 µm glass fiber filters (VWR Grade 693); 0.45 µm cellulose nitrate filters (Whatman Type WCN); 0.22 µm cellulose nitrate filters (Fisher Scientific). All filters were conditioned with distilled water (ca. 50 mL) and filtrate from the previous filter (ca. 50 mL) prior to sample collection. The 1.1 µm and 0.45 µm fractions were used for characterization studies (Chapter 4). The 0.22 µm sample (ca. 3 L) was further fractionated using an Ultrasette 1 kDa tangential flow filtration capsule (Pall Life Sciences) described below.

3.4.TFF system

The TFF system consisted of a Pall Ultrasette 1 kDa low protein-binding, modified polyethersulfone membrane (effective surface area 700 cm^2) contained in a styrene acrylonitrile outer housing and a Masterflex L/S peristaltic pump (Cole Parmer). The pump and filter were connected with Pharmed 16 tubing (Cole Parmer) and silicone tubing. Sampling mode (retentate returned to feed flask) was used to process the sample under the following conditions: feed inlet pressure 15–20 psi, retentate outlet pressure < 10 psi, retentate flow rate 1 L min^{-1}, and permeate flow rate 50 mL min^{-1}. The TFF system was cleaned prior to and after the experiment using 5 L distilled water and 0.01 M NaOH, respectively in recirculation mode for 2 h. After cleaning, the filter was conditioned using 5 L MilliQ water through both retentate and filtrate ports. 300 mL of filtrate was rejected prior to collection.

3.5.Multi-sparger system

A multi-sparger system consisting of two control (MilliQ water), two 1.5 µm replicates, and two 1 kDa replicates or two SS replicates was employed. The apparatus consists of a high-purity nitrogen gas stream pre-wetted via a pre-sparger delivered to a 6-port manifold (individually valved). Each port delivers ca. 50 mL min^{-1} nitrogen to a 1 L sparger (measured using electronic flow controller). Spargers were kept at 25 °C (±0.5 °C) via a circulating water bath. Spargers were spiked with 100 µL of the chlorobenzene mixture, mixed through shaking and allowed to equilibrate ca. 18-24 h in the water bath prior commencing experiments. XAD2 resins were prepared according to Chapter 3 guidelines. Prior to initializing experiments, XAD2 resins were spiked with the TBB internal standard and placed at the outlet of the sparger. Flow rates were corrected to 45 – 55 mL min^{-1} after changing each adsorbent (at 0.5 h intervals for 8 h) to allow for variability in flow characteristics given the shared manifold. XAD2 resins were capped using polyfilm and placed in sealed bags at 4 °C until extracted.

4. Analytical Methods

Analysis of all samples was carried out on a Varian 3600 GC equipped with split/splitless injector, a 30 m X 0.32 mm fused silica DB-5 column with a 0.25 µm film thickness (J&W Scientific) and an ECD detector. The injector was maintained at 250 °C with a flow rate of 2 mL min^{-1} He. A 1 µL injection was made into a 253 µm liner and the column was held at 140 °C for 2 min. Subsequently, the column was raised to 192 °C at 6.5 °C min^{-1} ramp. The makeup flow rate was 29 mL min^{-1} N_2 and detector temperature at 250 °C. The limit of detection (LOD) is defined as the minimum amount of analyte which produces a peak with a signal-to-nose ratio equal to 3. A PeCB standard was injected prior to and post all experimental runs as quality control and expected to fall within a standard deviation of standard curve values.

5. Results and Discussion

5.1.Method validation

Figs. 2–4 exhibit representative results for the 1,2,4,5-tetrachlorobenzene 1 kDa analysis only. A cumulative mass purged versus time figure is shown in Fig. 2. As shown previously (Chapter 5), the curves change slope at the 6 h point, which is when the dissociation rate becomes relevant compared to the volatilization rate. Variation between the three experiments is apparent early in the sparging process, as the control sparger mass purged increases faster than the 1 kDa and 1.5 µm curves. Of interest is the 1 kDa curve, which is markedly lower than the control spargers. This trend exists for each of the chlorobenzenes and indicates that the COC below 1 kDa is a significant source of sorption for the CBs.

To determine the k_v constant, control spargers total mass sparged were plotted using eq 2 considering a 1 L total sparger volume (Fig. 3). As shown by the linear regression coefficients ($R^2 = 0.994$ and $R^2 = 0.985$), the sparging rate was linear over the initial 6 h period. H was calculated using eq 3 and is included in the average H (Table 1) considered over multiple experiments previously. Using the k_v value, C_t versus $e^{-k_v t}$ is shown in Fig. 4. As with Fig. 3, the linear regression coefficients ($R^2 = 0.978$ and $R^2 = 0.978$) indicate sparging was linear

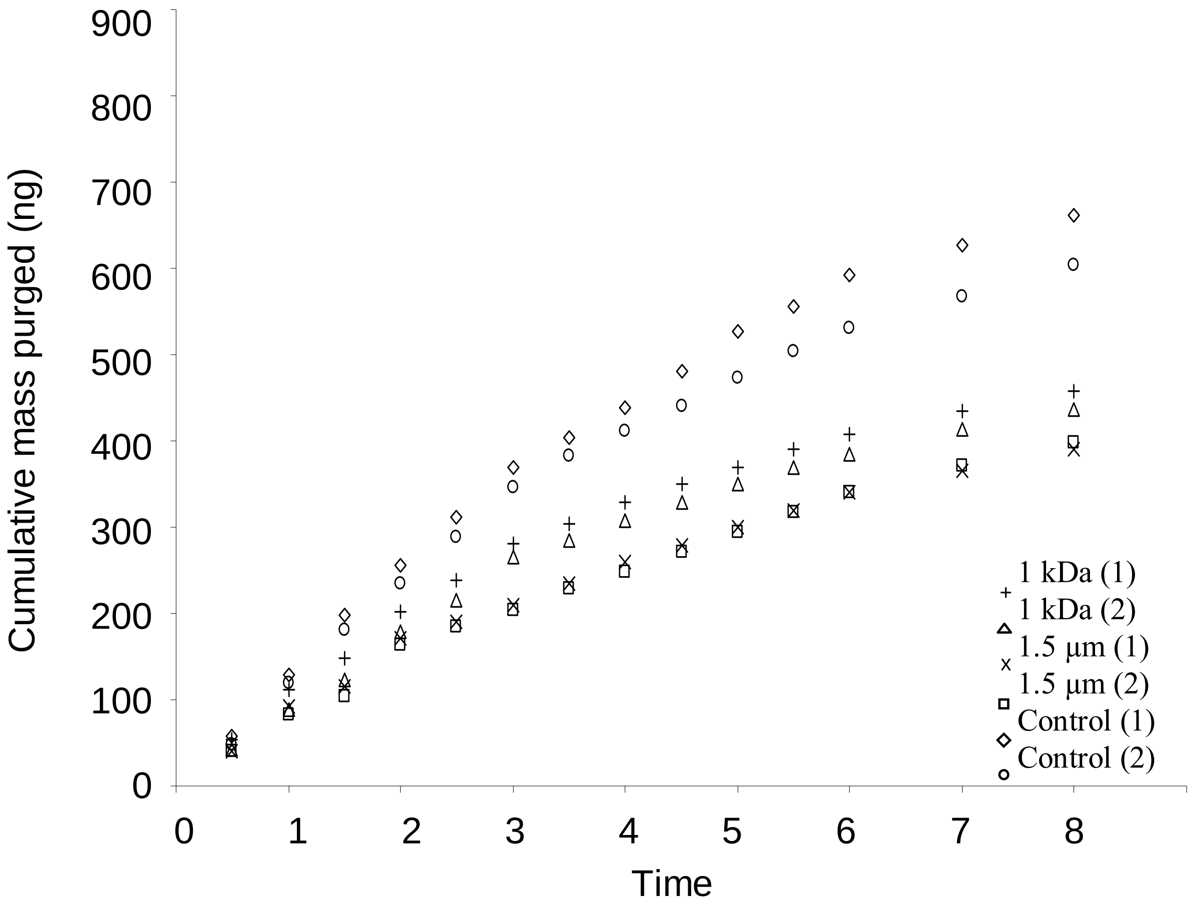

Fig. 2: Depletion curves for a representative experimental run and chemical (TeCB).

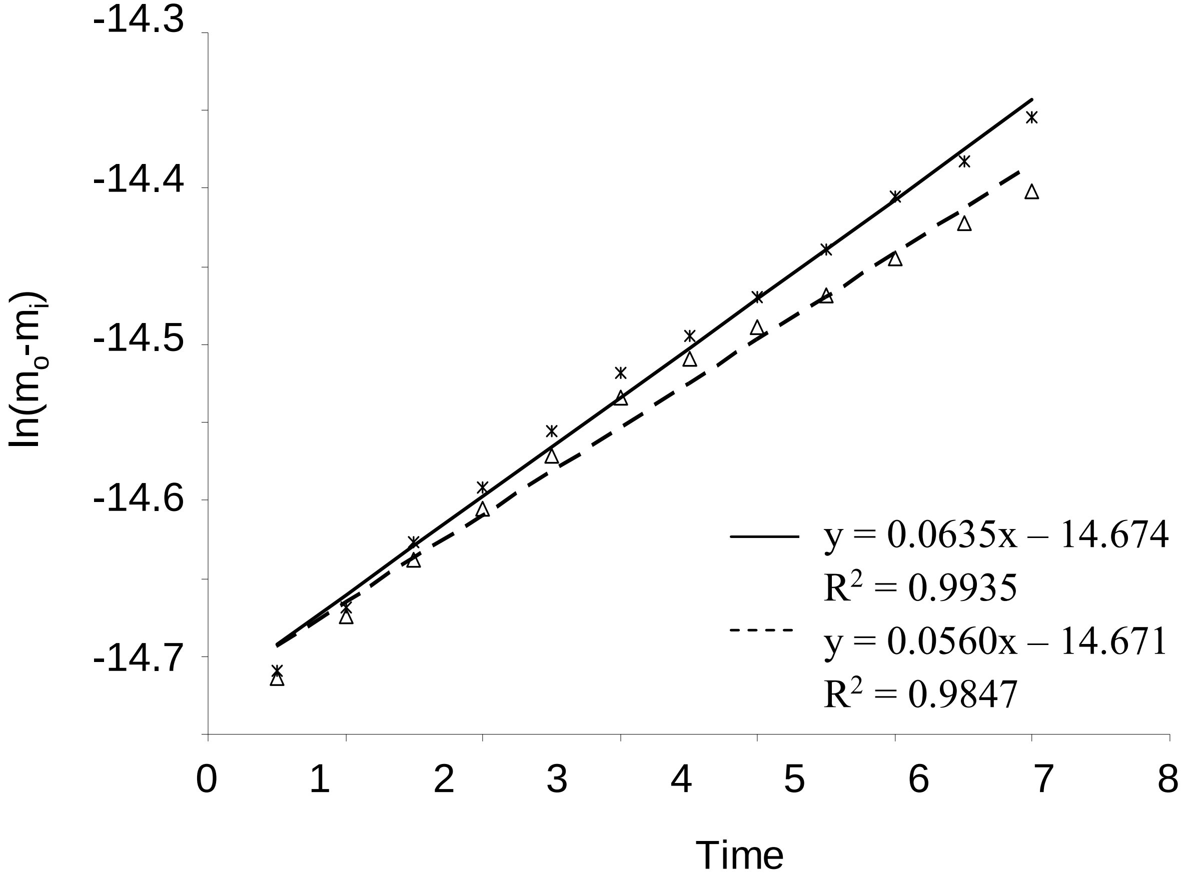

Fig. 3: Least squares linear regression of the natural logarithm of initial (spiked) minus measured cumulative mass (trapped) over time for control spargers initial slope (TeCB).

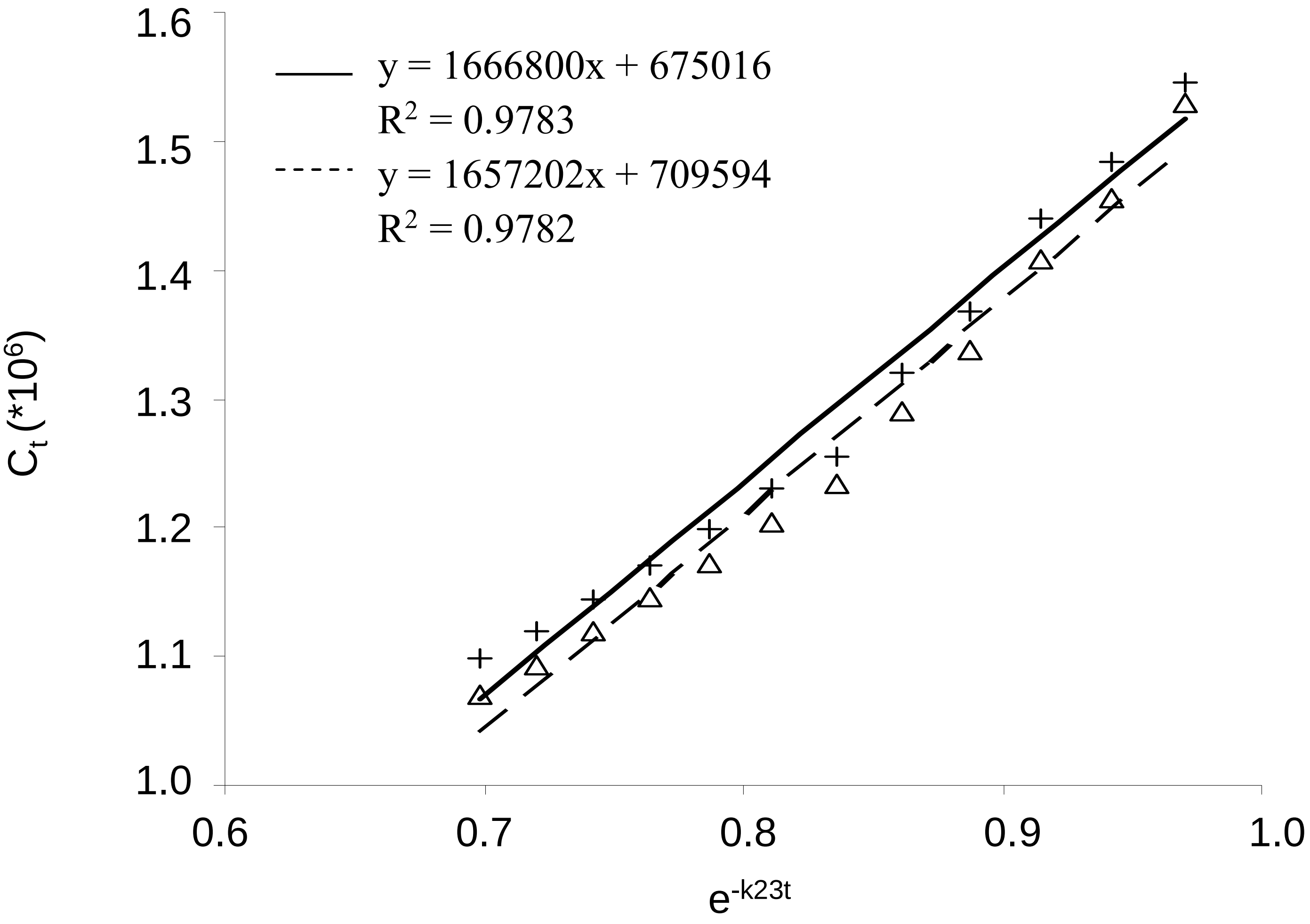

Fig. 4: Least squares linear regression of the total concentration versus exponential slope of control spargers over time for treatment spargers over the initial slope period (TeCB).

over the time period. Using eqs 4-7, the K_{COC} and values may be determined (Table 2) and are discussed below.

5.2. 1 kDa versus reference logK$_{oc}$ values

TeCB $\log K_{COC}$ average (4.30) and range (4.27 – 4.33) both are within the reference ranges for soils (2.79 – 4.5) and sediments (3.36 – 5.10), but are slightly higher than suspended particulates measurement (3.94) and humic acids (Table 2). PeCB $\log K_{COC}$ average (4.36) and range (4.30 – 4.53) are in reasonable agreement with all reference ranges, being marginally lower or higher in all cases (Table 2). HCB $\log K_{COC}$ average (3.74) and range (3.55 – 3.89) falls within the wide $\log K_{oc}$ of soil references (2.56 – 6.00). Reference $\log K_{oc}$ ranges for sediments, suspended particulates, AHA and ground water are higher than the current study's average and range (Table 2).

Based on $\log K_{ow}$ values of 4.5, 5, 5.5 for TeCB, PeCB, and HCB (Table 1), it would be expected that $\log K_{COC}$ values would correlate to hydrophobicity, thus TeCB < PeCB < HCB. However, the current $\log K_{COC}$ values do not follow the expected pattern, with TeCB ~ PeCB > HCB. As shown in previous work (Table 2), the 1.5 µm fraction exhibited similar partitioning behaviour (with varying partitioning, discussed below); therefore mechanisms in which the current unexpected sorption behaviour to COC occur must be determined.

Physicochemical properties for both sorbate and sorbent are important in the determination of the HOC–COC sorption behaviour. Contrary to prior use of the K_{ow} parameter as the benchmark for partitioning behaviour of HOCs in many other media, the

Table 2: Summary of K_{DOC} values for 1 kDa, 1.5 μm^{t}, and > 1 kDa sparging results as calculated using the initial slope method.

	$\log K_{DOC}$			$\log K_{oc}$	
chemical	1 kDa	1.5 μm^{t} (total)	>1 kDa (corr.)*	reference range	
tetraCB	4.30	3.86	2.83	*Soils*:	2.79 – 4.5[a,b,c,d]
				Sediments:	3.36 – 5.10[b,e,f]
				Suspended:	3.94[g]
				Humics:	4.10 – 4.21[h,*]
pentaCB	4.36	3.89	3.09	*Soils*:	3.81 – 4.49[i,j]
				Sediments:	4.23 – 6.20[d,e,f,h,j,k,l,m,n]
				Suspended:	4.59 – 5.90[g,o]
				Humics:	4.50 – 5.13[h,p,*]
hexaCB	3.74	3.19	2.17	*Soils*:	2.56 – 6.00[a,c,d,j,q,r]
				Sediments:	4.80 – 6.70[d,e,f,k,l,m]
				Suspended:	4.89 – 6.50[e,g,o]
				Humics:	4.70 – 5.43[h,p,r,s,t,*]
				Ground water:	5.65[s]

[*] mathematical correction based on fraction masses.

[a]Briggs, 1981; [b]Schwarzenbach et al., 1981; [c]Walton et al., 1992; [d]Delle Site, 2001; [e]Oliver and Charlton, 1984; [f]Djohan, et al., 2005; [g]Masunaga, 1996; [h]Resendes et al., 1992; [i]Paya-Perez et al., 1991; [j]Wu and Gschwend, 1986; [k]Karickhoff and Morris, 1985; [l]Oliver, 1987a; [m]Schrap et al., 1994; [n]Cornelissen et al., 1997; [o]Oliver, 1987b; [p]Urrestarazu Ramos et al., 1998; [q]Rippen et al., 1982; [r]Enfield et al., 1989; [s]Freidig et al., 1998; [t]Yabuta et al., 2004.[*]McPhedran et al., 2011

current MWTP effluent organics must differ from other organics resulting in the current partitioning behaviours. Molecular mass, compound competition, and COC characteristics may impact the partitioning behaviour markedly based upon numerous studies in the literature discussing partitioning of various HOCs (Perret et al., 1994; Gustafsson et al., 2001; Ma et al., 2001; Drewes et al., 2002; Holbrook et al., 2004; Pan et al., 2007). Alternatively, differences in electronegativity and structural formation may also be considered as influences on partitioning properties.

5.3. 1 kDa versus 1.5 µm partitioning

The partitioning coefficient increases from 1.5 µm to 1 kDa for each of the chlorobenzenes (Table 2) by a factors of 0.47, 0.53, and, 0.55 log units for TeCB, PeCB, and HCB, respectively. Therefore, the 1 kDa fraction is both involved in chlorobenzene partitioning and exhibits greater partitioning coefficients for each chemical versus the total 1.5 µm fraction. Given the availability of both size fractions simultaneously, the intermediate fraction less than 1.5 µm and greater than 1 kDa can be determined using the partition coefficients and COC masses. As shown in Table 2, the partitioning to this size fraction was much lower than both the overall 1.5 µm and 1 kDa fractions.

In contrast to previous work (Backhus et al., 1990; Gustafsson et al., 2001; Backhus et al., 2003; Holbrook et al., 2004), partitioning to the under 1 kDa fraction (and arguably 500 Da fraction given the partitioning increase) does indeed occur and this physical limit cannot be considered as the threshold for ‘truly-dissolved’ for all chemicals. Gustafsson et al. (1997) suggested delineating the dissolved-colloidal boundary based upon a ‘chemcentric’ view. Clearly, a chemcentric view would more appropriately describe partitioning behaviour for a wide range of chemicals based upon total physicochemical properties rather than a more arbitrary physical size cut-off. Unfortunately, fractionation of colloids using current filtration techniques must improve to include smaller pore size ultrafilters. Filter size availability has historically been a limitation to determination of a truly-dissolved phase and this would appear to be no less the case when considering ultrafiltration technologies currently available.

Many studies have shown the omission of the smaller size fraction, such as a 1 kDa fraction, from partitioning behaviour experiments, which can result in erroneous partitioning coefficients (Backhus et al., 1990; Holbrook et al., 2004). For example, when the 1 kDa fraction is mathematically removed from total 1.5 µm fraction partitioning, there is an order of magnitude decrease in the partition coefficients for each chlorobenzene (Table 2). Clearly the partitioning behaviour is quite variable between different size fractions and must be considered for each size fraction independently. However, the importance of the lower size fractions may decrease with increasing molecular size rather than mass. Given the larger sizes of PAHs used in the previous studies, it can be suggested that the use of a 500 – 1 kDa may be appropriate for these compounds. Alternatively, many such studies have used the 'truly-dissolved' fraction found in ultrafiltration filtrates for sample dilution. Such use should only be considered with consideration of possible experimental artefacts created from partitioning to the filtrate.

6. Environmental Significance

Figure 1 shows the various organic constituents in a MWTP. Given the wide range of constituents, and potential for variable partitioning behaviours, greater study is needed in the determination of chemical fate through the MWTP. The current study emphasizes the need for a more robust and consistent delineation of truly-dissolved, colloidal, and suspended solids beyond the historic aquatic colloids benchmark and with a chemcentric viewpoint not determinant on only filter fractions such as a 0.45 µm cut-off which has been extensively used (Shon et al., 2006). Further physicochemical determinations of COC found in the MWTP are needed to discover potential mechanisms behind effluent partitioning behaviours.

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CHAPTER 7

Discussion

1. General Discussion

The importance of determination of the fate and transport of chemicals of concern (CHCs) throughout municipal wastewater treatment plant (MWTP) processes is of utmost concern for the safety of both human and environmental health. An examination of the fate of historic and emerging contaminants in the MWTP process allows for the understanding and prediction of potential environmental loadings and subsequent risk assessment. The major processes considered for the fate of chemicals during the commonly used activated sludge type secondary MWTP are shown in Fig. 1. The partitioning to solids commonly considered and accounted for is that to solids larger than 1.5 µm, called suspended solids. Municipal wastewater has significant amounts of colloidal organic matter (solids < 1.5 µm) particularly in the early stages of the treatment process. Partitioning to these solids is poorly understood and typically ignored in experimental analysis.

The investigation started with selection of methods for experimental determination of partitioning. Amongst the traditional methods, gas sparging was chosen since it allows simultaneous calculation of Henry's law gas constant using colloid-free water, permits measurement of the freely dissolved chemical, is sensitive enough for determining sorption and desorption rates, and has been extensively used in the literature. More recently, headspace solid-phase microextraction (HS-SPME) has been developed with many of the same advantages as gas sparging making it potentially useful for the current study. However the methodology for application of HS-SPME for partitioning experiments is not well-tested or developed, especially for MWTP-type samples. If found to be useful, advantages over long column include smaller sample volume which

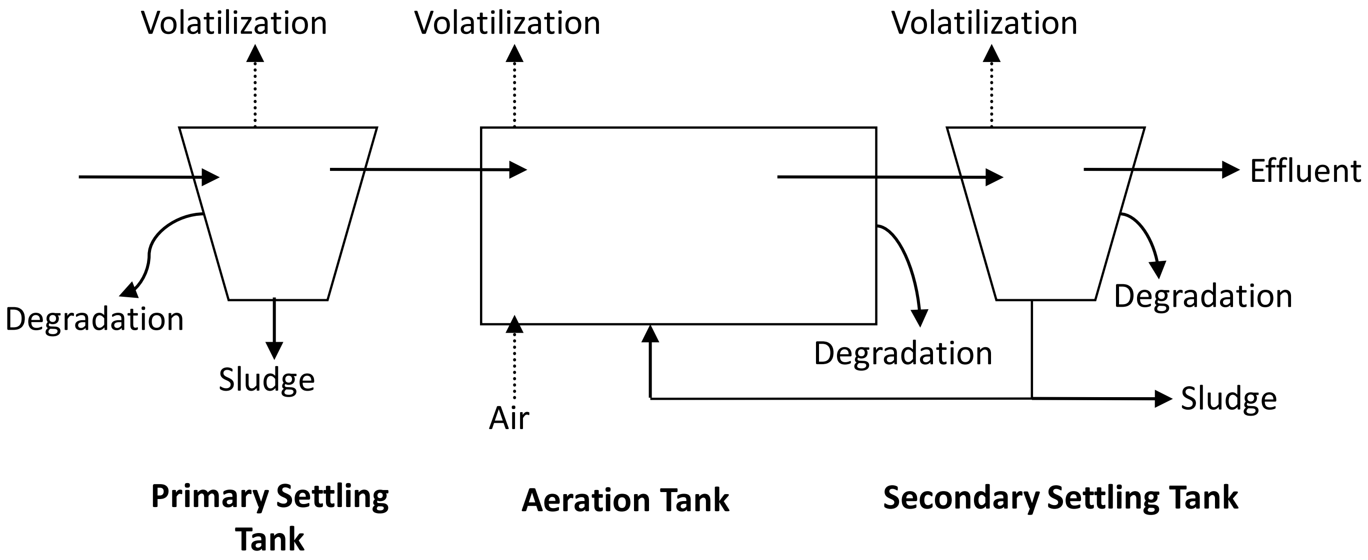

Fig. 1: Schematic of a typical activated sludge wastewater treatment plant (WWTP) with chemical fate and transport processes.

decrease processing times, shorter experimental duration with high SPME phase chemical capacity, and eliminate the need for sample extraction since the fibre is used directly in GC detection. It was therefore chosen for further investigation and development of a methodology for conducting the experiments prior to use in partitioning experiments. HS-SPME was first used in Chapter 2 to determine the effects of co-solvent on the apparent solubility on a suite of three chlorobenzenes (CBs). Results indicated that methanol concentrations up to 1% had no effect on the freely dissolved chemical. However, given potential interaction of methanol with colloids, a lower concentration (0.01%) was considered for partitioning experiments. Despite spending significant time and effort, application of HS-SPME for partitioning experiments was unsuccessful primarily due to significant loss of chemical mass from the small vial system. Efforts to identify the sources for this loss and eliminate them were unproductive. HS-SPME was abandoned for determination of partitioning and the gas sparging technique was used exclusively for the remaining experiments.

Henry's law constant (HLC) is a parameter used to describe the mass transfer of chemical between water and air. HLC is needed for determination of partitioning in experiments, however, has a wide range of variability in the literature for the CBs. Hence selection of values from literature is difficult as well as inappropriate for use in the partitioning experiments of the current study. Chapter 3 HLC values were determined using the current gas sparging technique and served as control spargers for the remaining partitioning experiments. Calculated HLCs for the CBs were 56.5, 33.3, and 29.9 Pa m^3 mol^{-1} for 1, 2, 3, 5-tetrachlorobenzene (TeCB), pentachlorobenzene (PeCB), and hexachlorobenzene (HCB), respectively. During the course of the experiments, the effect of sorption to glass surfaces was realized via non-linear volatilization rate in control spargers. Given the robustness of the sparging experiments this non-linearity was readily identifiable via three distinctive phases of sparging including initial slope, transitional, and steady state regions. In the initial slope region the volatilization rate is dominant, as the chemical is stripped from the water column desorption processes and volatilization rates converge in the transition region, and in the steady state region desorption rates becomes greater than volatilization rate. Given these observations, only the preliminary linear sparging zone was used to determine HLC, while the remaining phases will be valuable for determination of desorption rates in partitioning experiments. Although contribution of glass sorption has been recognized in gas sparging experiments, its contribution has not been not been properly quantified. Through use of the entire sparging region rather the initial slope previous researchers may have inaccurately determined HLC using the gas sparging technique.

Prior to the commencement of partitioning experiments methods of fractionation and characterization of colloids were considered. An important aspect of fate and transport of CHCs within a MWTP is partitioning of CHCs to various size fractions of organic matter. Fractionation of colloids was accomplished by the use of typical membrane and ultra-filtration techniques. Results of the fractionation indicated that ca. 70% of the MWTP primary effluent sample was found in the smallest size fraction (1 kDa). Given the large quantity of colloids in this size fraction further use in partitioning experiments was considered necessary to determine the fractions' role in partitioning. Previous studies neglected this size fraction since colloids under 1 kDa were considered truly-dissolved and unable to bind chemical. Additionally, colloids in natural organic matter and Aldrich humic acids exhibit much less mass under 1 kDa (under 10%) indicating significant variation with MWTP colloids. Characterization methods considered included UV absorbance and ^{1}H NMR. While UV absorbance is a typical method, the ^{1}H NMR technique was developed given the limited application in MWTP analysis and poor sensitivity and resolution of prior studies. Results of UV absorbance indicated a linear relationship between colloid concentration and absorbance. ^{1}H NMR results showed that the experimental development was successful in increasing sensitivity and resolution through sample processing which did not negatively impact sample integrity. Further study of ^{1}H NMR using the developed technique may be useful in determination of specific compounds which can aid in the determination of partitioning mechanisms.

Given the positive results of the Chapter 2, 3, and 4 studies, partitioning experiments were conducted using MWTP primary effluents. In a MWTP suspended solids are considered as the particles captured using a 1.5 µm filter. Solids passing this filter are dissolved or colloidal organic matter, which has typically not been considered relevant in transport and fate of CHCs. Given that ca. 50 mg L^{-1} of colloids (as organic carbon) are present in the primary effluent, lack of consideration of potential partitioning to this fraction is unadvisable. It was therefore determined that the entire 1.5 µm fraction be used in the determination of partitioning of CBs. Calculated partitioning results were $\log K_{COC}$ 3.86, 3.89, and 3.19 for TeCB, PeCB, and HCB, respectively. These partitioning results (TeCB~PeCB>HCB) did not conform to expectations based upon hydrophobicity (TeCB<PeCB<HCB) and potential mechanisms for these differences were discussed. Aldrich humic acids were used as a standard reference with results

following the expected trends based on hydrophobicity. The lack of correlation with hydrophobicity (determined by K_{OW}) in the current study was unexpected given numerous correlations found in the literature. However, this result illustrates the differences between MWTP organics and both natural and Aldrich humic acids and the need for further study of this variation. Additionally, the dependence of partitioning on chemical hydrophobicity has been recently questioned. As found in Chapter 3, sparging results exhibited three distinct phases, initial slope, transition, and steady-state. The steady-state region is indicative of desorption from colloids (and glass surfaces) and may be used to determine desorption and sorption rates. The desorption rates were within an order of magnitude of literature values. Sorption rates indicated that steady-state was reached by all samples in the allotted 18-24 h equilibration period. Overall partitioning to colloids was significant and they should not be omitted in determination of fate and transport processes in a MWTP.

With the determination that partitioning to colloids is significant the role of the smallest size fraction (< 1 kDa) was considered. Given the results of Chapter 5 indicating the large percentage of colloids in this size fraction (ca. 70%), ad hoc dismissal of the importance of this fraction in partitioning is erroneous. Despite this assertion previous researchers considered colloids under 1 kDa as being truly-dissolved and unable to partition with chemicals. This assertion has been previously untested and was considered due to the current limits of filtration technology available. To test this assumption, the Chapter 6 study used the less than 1 kDa fraction for partitioning experiments. Calculated partitioning results were $\log K_{COC}$ 4.30, 4.36, and 3.74 for TeCB, PeCB, and HCB, respectively. As for the 1.5 µm fraction, these partitioning results

(TeCB~PeCB>HCB) did not conform to expectations based upon hydrophobicity (TeCB<PeCB<HCB). For each of the CBs the partitioning increased versus the 1.5 µm fraction, exhibiting that not only is the 1 kDa involved in partitioning, it has a greater affinity as well. Although previous research involved larger chemicals which may not partition to the smaller size fractions, omission of this size fraction or neglect of its potential role may be in error.

2. Engineering Significance

CHCs within the MWTP process can be found freely-dissolved, bound to colloids, and bound to solids. CHCs bound to solids in the MWTP will settle throughout the MWTP in various processes. However, CHCs found freely-dissolved and as CHC–colloid can be found in MWTP effluents and released into the receiving environments. This thesis concentrated on the colloidal COC present in raw municipal wastewater which is carried through the primary treatment process (Fig. 1) of a typical secondary municipal wastewater treatment plant. The investigation of the fate and transport of CHCs in this stage is important since the colloid associated CHCs are unavailable for sedimentation, volatilization, and/or biodegradation, and carried through with the effluent to the secondary treatment stage of the MWTP process. This is especially relevant for HOCs, such as CBs, which have low volatilization and degradation rates and high octanol water partitioning coefficients which indicate high affinity for organic matter (or carbon). Additionally, the higher OM concentration of this stage allows for direct use of samples in laboratory experiments, thus negating potential effects of sample concentration using filtration techniques that lead to erroneous partitioning results due to removal of relevant

OM. Partitioning coefficients found in this primary treatment tank process may then be considered as a valid first approximation for use in the remaining MWTP processes in STP modelling until further research on these stages is completed.

In the present research, partitioning of a suite of CBs to colloidal organic matter in the primary effluent of a MWTP wastewater was investigated. This partitioning was found to be significant and must be considered in the fate and transport of CBs (and other CHCs) in the MWTP. To assess the potential impact of this partitioning to the primary stage of the treatment process, typical MWTP characteristics and primary treatment performance values were used (Table 1). The primary stage distribution was considered using a mass balance with total chemical input and outputs including primary effluent and sludge. Volatilization and degradation processes were negligible for the CBs and were not considered further. Partitioning to solids was determined using H and K_{ow} according to the relationship $K_p = (0.8 + 0.2K_{ow})$. A sample calculation using 1,2,4,5-TeCB is included in the Appendix.

Results from this analysis indicate the overall contribution of including colloidal partitioning. Increases in the apparent solubility (freely dissolved plus colloid-bound) of each chemical increase 26.7, 28.0, and 7.6% for TeCB, PeCB, and HCB, respectively. Given the current study results deviating from expected hydrophobicity related partitioning, the increase in HCB was markedly lower than both TeCB and PeCB. Results from this analysis are approximate given the solids partitioning is derived from the octanol water partitioning relationship (K_{ow}) which may not truly represent actual partitioning to MWTP solids.

Table 1: Typical MWTP properties and input chemical properties used to determine mass balance in the primary stage treatment tank.
*ca. COC determined in current study.

parameter	variable	units	value
influent	flow	m^3 h^{-1}	1000
	TSS	g m^3	200
	COC*	g m^3	50
primary tank	solids removal	%	60
	TSS	g m^3	50000
chemical properties	concentration	mol h^{-1}	1
	H	Pa m^3 mol^{-1}	
	TeCB		56.5
	PeCB		33.3
	HCB		29.9
	$logK_{ow}$	unitless	
	TeCB		4.5
	PeCB		5.0
	HCB		5.5
	$logK_{COC}$	unitless	
	TeCB		3.86
	PeCB		3.89
	HCB		3.19

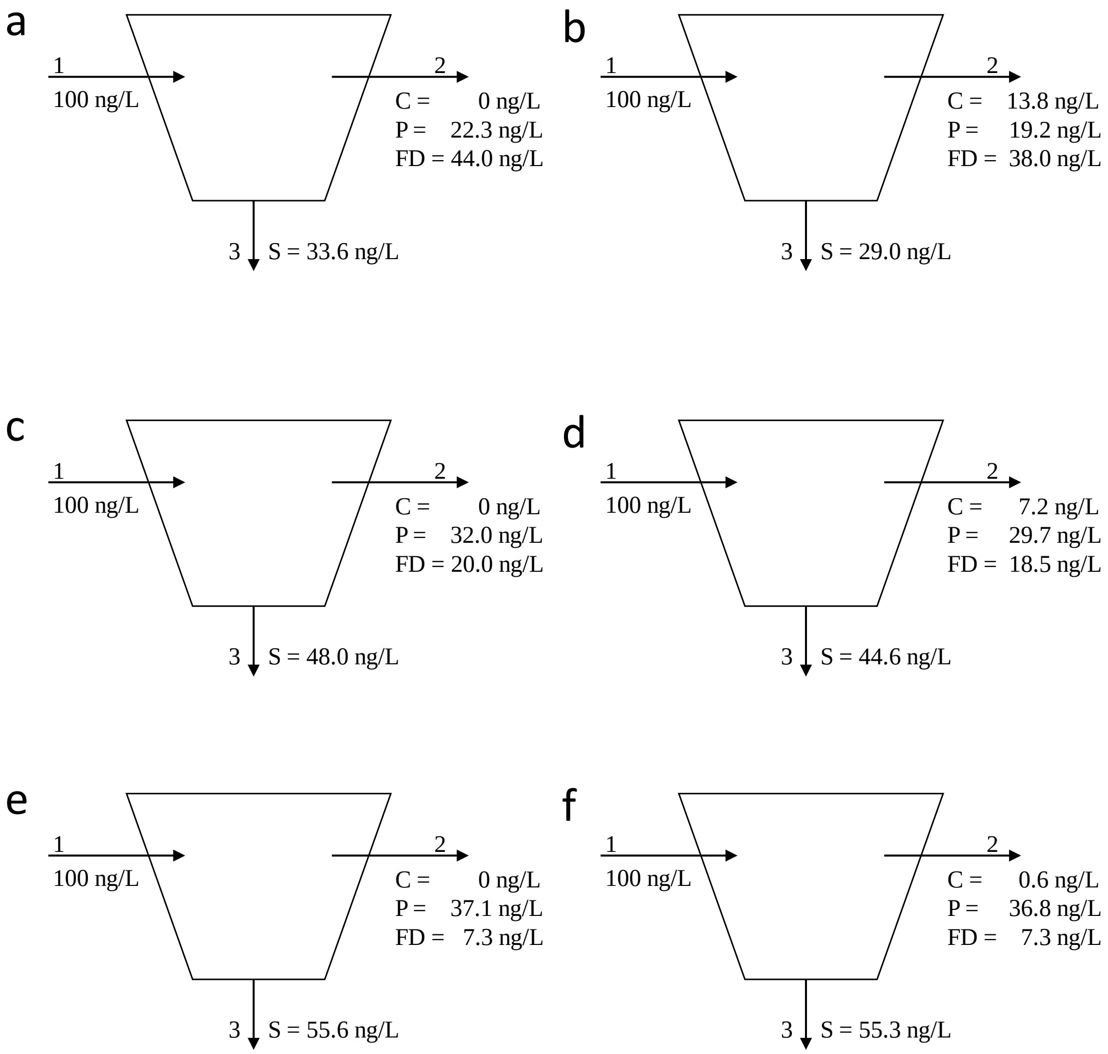

Fig. 2: Mass balances of primary stage tanks. (a,c,e) represent absence of colloid partitioning. (b,d,f) represent inclusion of a colloid partitioning parameter. S = solids; C = colloids; P = particulates; FD = freely dissolved.

3. Recommendations for Future Work

- Determination of a K_{COC} parameter of raw wastewater influents for other HOCs and chemicals of emerging concern should be considered to improve understanding of chemical fate and transport throughout the MWTP process.
- The COC concentration of secondary effluents and final effluents reduces substantially as compared to the primary treatment effluents. Further study to determine the K_{COC} for HOCs in the remaining MWTP compartments is needed.
- Assessment of HOC partitioning behaviour is invaluable in the evaluation of MWTP models used to determine chemical fate and transport. Current models should be modified to include a K_{COC} parameter which can be easily implemented for the primary treatment tank process. Additionally, more research is needed before consideration of a K_{COC} parameter for the secondary biological treatment process.
- Cross-flow ultrafiltration is a valuable method for fractionating MWTP flows. Given the importance of the 1 kDa fraction in the current study, ultrafiltration of COC to determine the magnitude of the smallest COC size fractions must be considered for all COC studies.
- The NMR technique developed should be considered for future MWTP research to further develop the understanding of the correlation between functional groups on partitioning behaviour. These correlations may then be used for determination of fate and transport especially in MWTP modelling.
- In subsequent municipal wastewater investigations a 1.5 µm filter should be used as the delineation between suspended solids and colloidal matter. This filter size is historically used in MWTP solids analysis and represents an excellent choice for the

suspended-solid to colloidal cut-off. By using the same size fraction amongst studies more direct comparisons are readily made.

- HOCs are released into aqueous environments via MWTP effluents as freely-dissolved chemical and HOC-COC complexes. The understanding of the potential for HOCs, and all CHCs, to interact with COC in the natural environments is needed to predict the fate and transport of chemical as well as their impact on aquatic organisms.

APPENDIX

Mass Balance Calculation (1,2,4,5-TeCB example)

OVERALL Mass Balance

Fugacity	fp=	E/(D2+D3+Dpv+Dpb)
Stream 1 input	E=	1 mol/h
Stream 2 processes	D2=	GW2*ZW+GS2*ZP+GCOC2*ZCOC
Stream 3 processes	D3=	GS3*ZP+GW3*ZW
Volatilization	DPV=	KLC*AP*ZW
Biodegradation	DPB=	KBP*VP*ZW

Fugacity capacity equations

Liquid	ZW=	1/H
Solids	ZP=	ZW(0.8 +0.2KOW)
COC	ZCOC=	ZW*KCOC

Input values

Chemical influx	E=	1	mol/h
Liquid mass flow rate	GW2=	997.6	m3/h
TSS mass flow rate	GS2=	0.08	m3/h
COC mass flow rate	GDOC2=	0.05	m3/h
Sludge solid mass flow rate	GS3=	0.12	m3/h
Liquid mass transfer coefficient	KLC=	0.025	m/h
Tank area	AP=	266.7	m2
Biodegradation rate	KBP=	6.93E-06	/h
Tank volume	VP=	1013.46	m3
Henry's law constant	H=	5.65E+01	Pa*m3/mol
Octanol/water partition coefficient	KOW=	31623	
COC/water partition coefficient	KDOC=	7244	

Results

fp=	2.15E-02	Pa
D2=	3.30E+01	mol/h/Pa
D3=	1.35E+01	mol/h/Pa
DPV=	1.18E-01	mol/h/Pa
DPB=	1.24E-04	mol/h/Pa
ZW=	1.77E-02	mol/m3/Pa
ZP=	1.12E+02	mol/m3/Pa
ZCOC=	1.28E+02	mol/m3/Pa

		mass %
FD	(GW2*ZW)	38
P	(GS2*ZP)	19
C	(GCOC2*ZCOC)	14
S	(GS3*ZP+GW3*ZW)	29

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