Novel Applications of the Waterloo Membrane Sampler (WMS) in Volatile Organic Compound Sampling from Different Environmental Matrices

by

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DECLARATION

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

I understand that my thesis may be made electronically available to the public.

ABSTRACT

The Waterloo Membrane Sampler (WMS) is a polydimethylsiloxane (PDMS)-based permeation passive sampler developed at the University of Waterloo. This sampler has found numerous applications in the sampling of volatile organic compounds (VOCs) from air and soil gas. In the presented thesis, studies were conducted to expand the WMS applicability to different environmental matrices. In the first part of this work, a modified version of the sampler, with a smaller area of the sampling surface, was calibrated towards seventeen VOCs listed as sources of concern in guidance documents for vapor intrusion. The calibration constant values obtained at different exposure periods demonstrated high reproducibility and independency of the exposure time. Furthermore, the application of the WMS for VOC sampling from groundwater was examined. This study involved seven VOCs considered as important groundwater pollutants. The performance of the sampler was examined at different concentration levels and for different exposure times. The effects of the sorbent type and bubble formation at the surface of the membrane on the sampling efficiency were evaluated in order to optimize the performance of the WMS. A hypothesis regarding the calibration constant values in water sampling compared to their values in air sampling was examined. The WMS demonstrated linear uptake of the targeted compounds over the studied periods of time and at different concentration levels. Very low detection limits were achieved for all studied compounds. The calibration constant values for the sampler towards the studied compounds were measured with a reasonable reproducibility. Nonetheless, the experimental values of the calibration constants in water sampling did not comply with the theory. Furthermore, a new method of bulk soil sampling was tested. In this approach, the soil sample is enclosed in a container along with the WMS placed in the headspace of the sample. The capability of the WMS to perform exhaustive extraction of volatile organic

compounds trapped in the sample was tested in this case. Two compounds, TCE and PCE were used as model compounds to test the introduced method. The initial experiments involved sampling from spiked sand soil as the simplest scenario. The experimental setup was evaluated and modified accordingly to achieve the desired extraction. The effects of the exposure parameters on the extraction efficiency were examined through experimental design starting with extraction from sand followed by extraction from a soil with a high organic content. The three-factor factorial design used for this purpose included the three factors: temperature, water content, and exposure time. The results demonstrated high extraction efficiency achieved when sampling from sand and lower extraction efficiency when sampling from the soil with a high organic content. The recovery was enhanced to a large extent in the latter case at a higher temperature with very low detection limits. The results presented in this thesis indicate that the WMS can be a potential universal tool for sampling from all environmental matrices in vapor intrusion investigations.

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DEDICATION

This thesis is dedicated to my children Tarek, Ahmad, Ali, and Amer who took part in my journey with this thesis. The warmth of their hearts and the brightness of their eyes have always been a great support to me.

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LIST OF ABBREVIATIONS

ASE - Accelerated Solvent Extraction

BTEX - Benzene, Toluene, Ethylbenzene, and Xylenes

ECD - Electron Capture Detection

EPA - Environmental Protection Agency

FID – Flame Ionization Detection

FOCS - Fiber Optic Chemical Sensor

GC - Gas Chromatography

LDPE - Low-Density Polyethylene

LTPRI - Linear Temperature Programmed Retention Index

MAE - Microwave Assisted Extraction

MS - Mass Spectrometry

OVM - Organic Vapor Monitor

PCE - Tetrachloroethylene

PDB - Polyethylene Diffusion Bag

PDMS - Polydimethylsiloxane

PID - Photoionization Detection

P&T- Purge and Trap

PTFE - Polytetrafluoroethylene

PUF - Polyurethane Foam

SFE - Supercritical Fluid Extraction

SPMD - Semipermeable Membrane Device

SPME- Solid-Phase Microextraction

TCE - Trichloroethylene

TFME - Thin-Film Microextraction

TWA – Time-Weighted Average Concentration

VOC - Volatile Organic Compound

WMS - Waterloo Membrane Sampler

1. CHAPTER 1: INTRODUCTION

1.1. Volatile Organic Compounds (VOCs)

Volatile organic compounds (VOCs) are considered environmental pollutants of prime concern in all environmental media: air, water and soil. According to the Environmental Protection Agency (EPA) in the United States [1], volatile organic compounds are defined as "any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions, except those designated by EPA as having negligible photochemical reactivity". Other definitions of VOCs are based on the compound volatility. For example, the European Union considers a compound a VOC when its vapor pressure at 20 °C is above 10 Pa, while ASTM test method D3960-90 defines VOCs as organic compounds with vapor pressure values equal to 13.3 Pa or greater at 25 °C [2].

Various classes of important chemicals are identified as VOCs. Examples of these classes are aliphatic hydrocarbons such as hexane and pentane; aromatic hydrocarbons such as benzene and toluene; cyclic hydrocarbons such as cyclohexane; and halogenated organic compounds such as tetrachloroethylene and dibromochloromethane. In fact, this category of organic compounds consists of chemicals from most chemical groups: ketones, esters, aldehydes, alcohols, chlorofluorocarbons, amines, etc. [3]. VOCs are components of petroleum derivatives such as benzene, toluene, ethylbenzene, and xylenes (BTEX). They are also used in agricultural products. 1,4-Dichlorobenzene and 1,2,4-trichlorobenzene, for example, are used as herbicides; chloroform and 1,3-dichloropropene are used as fumigants, while xylenes are used as solvents for pesticides [2, 4]. Other sources of VOCs include paints, solvents, adhesives, refrigerants,

aerosol sprays, cleansers, disinfection byproducts, deodorants, etc. For instance, tetrachloroethylene (PCE) is used as industrial solvent, and trichloroethylene (TCE) is used as degreaser [2]. VOCs can also migrate from polymers such as poly(ethylene terephthalate) (PET) used to store bottled water, leading to contamination of the enclosed water with carbonyl compounds (mainly acetone, acetaldehyde and formaldehyde) [5]. VOCs are also produced naturally [2]; for example, the presence of 2-methylisoborneol (MIB) and geosmin, which cause odors in drinking water, has been related to the presence of *actinomycetes* or their metabolites, in addition to the presence of cyanobacteria and fungi [6].

Detrimental health and environmental effects are attributed to exposure to these contaminants. Health effects vary according to the toxicity level of the contaminant, from irritation, headaches or nausea to more serious effects such as damage to the kidneys, the liver or the central nervous system. Some VOCs are also known to be carcinogenic and mutagenic, while many show bioaccumulation and persistence [2, 4]. Many VOCs contribute to processes such as reduction of the stratospheric ozone, formation of tropospheric ozone, and formation of photochemical smog [2]. VOCs are also classified as a group of the most common pollutants in ground water, which contributes not only to odor and taste problems, but also to toxic effects [2]. BTEX are considered important pollutants in ground water due to their toxicity and aqueous solubility, in addition to other VOCs such as chlorinated solvents [7].

1.2. Vapor Intrusion

Vapor intrusion is the process of contaminant migration from the subsurface into the indoor air of overlying buildings through openings in the basement or in the foundations [8], as shown in Figure 1. These contaminants are vapors emitted from volatile chemicals present in contaminated soil or groundwater [9]. The contamination of these sources results from

improperly disposed of wastes, accidentally spilled chemicals, substances leaking from storage tanks, etc. [8]. An escalating concern has been raised about potential risks to human health posed by these intruding chemicals. Therefore, many studies have been conducted in order to provide an accurate description of risks and an effective method of indoor air assessment.

Although indoor air monitoring can be achieved through direct exposure of samplers to the indoor air, another line of evidence is also available through groundwater and soil gas sampling with a proper estimation of the attenuation factor [10]. This line minimizes background contamination influence caused by additional sources, such as chemical products used for building or cleaning purposes, or outdoor air contamination [10]. An assessment of soil gas concentrations in a vertical profile also provides valuable information about the transport of contaminants between the source and the indoor air.

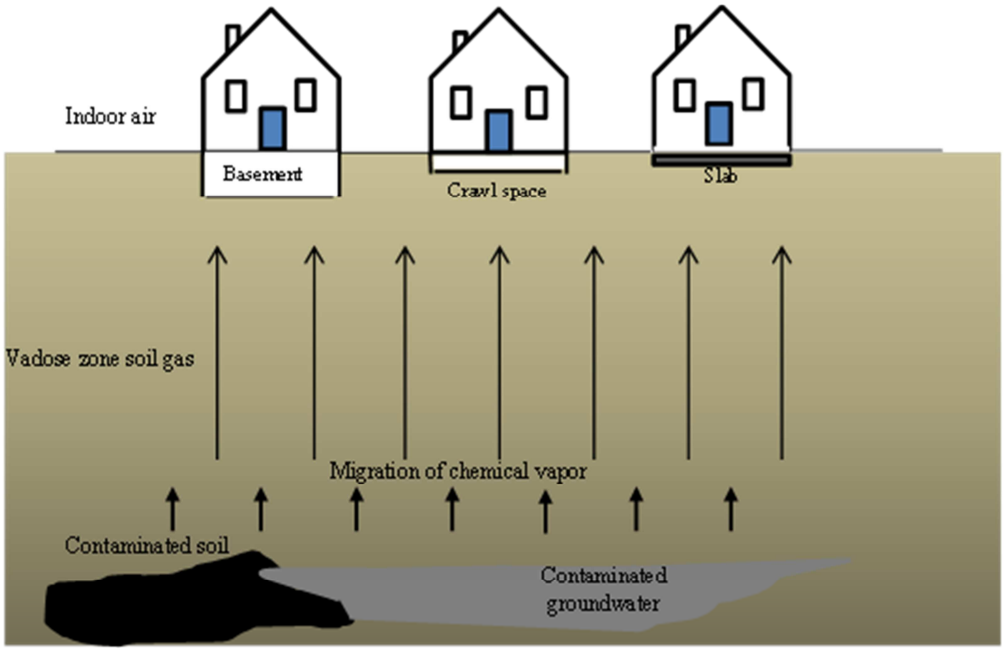

Figure 1-1- Vapor intrusion pathway (based on ref. [9])

1.3. Sampling Techniques

1.3.1. Active Sampling

Sampling and sample preparation are challenging steps in the process of monitoring VOCs in the different compartments of the environment: air, water and soil. A reliable sampling method produces representative samples of the studied medium and reflects concentration fluctuations in space and time [11]. A common method of sampling relies on the active approach, in which a large number of samples are taken during the monitoring period.

1.3.1.1. Sampling from air and soil gas

In active sampling from air, air samples are collected in polymer bags (e.g. Tedlar bags [12]) or inert containers by means of a pump [13]. This method of sampling is referred to as the whole air sampling; however, VOCs can be trapped separately in a sorbent medium [11]. In this case, a known volume of the studied air is pumped through an inert tube packed with a solid sorbent, or an impinger with an enclosed liquid [14]. When soil gas is sampled, the sample is collected by vacuum application at the distal end of a probe installed in the studied location [15]. The samples are collected into gas-tight syringes, Tedlar bags, glass cylinders, Summa canisters, or sorbent tubes [15].

After sampling, laboratory-based analysis is usually conducted. Air samples are introduced to gas chromatographs (GC) for separation. When preconcentration of the analytes is necessary, cryogenic techniques can be used [12] to focus the contaminants and enhance the sensitivity of the method. When sorbent tubes are used to trap the analytes, the extraction of these analytes before the analysis is achieved either by heating the sorbent (thermal desorption) or by adding a solvent (solvent desorption) [14]. The selection of the desorption method is based

on the type of the sorbent used in sampling; for example, graphitized carbon and Tenax® TA are desorbed thermally, while activated carbon-based sorbents and porous polymers are desorbed using solvent desorption [14]. After separation in GC, mass spectrometry (MS), flame ionization detection (FID) or electron capture detection (ECD) are usually used for VOCs [14].

On-site methods for real-time evaluation of airborne VOCs are also available. These methods include photoionization detection (PID) and flame ionization detection (FID), which are used for total contaminant concentration measurements [14]. Other tools for real-time measurements are also available but are more expensive and complex [14]. These techniques include differential optical absorption spectroscopy (DOAS), low-pressure chemical ionization/tandem mass spectrometry (LPCI-MS^2), atmospheric pressure chemical ionization/ tandem mass spectrometry (APCI-MS^2), and proton-transfer reaction MS (PTRMS) [16].

The requirement for a pump in active sampling, in addition to other sampling equipment, adds many disadvantages to this method. These disadvantages are due not only to the high cost of the process, but also to the need to provide a power source, to monitor the sampling process, and to move the pump and other equipment from place to place as needed [14]. Nevertheless, active sampling is still a desirable option because of the sampling rate control and the sampling rapidity obtained in this technique [17].

1.3.1.2. Sampling from water

Collecting discrete grab water samples (bottle samples) at a given time is the method on which most water quality monitoring programs rely [18]. In this method, large volumes of water samples are needed in most cases, where trace levels of contaminants are examined [18]. Since the analysis of these samples provides a snapshot of pollutant concentrations at a given time,

fluctuating concentrations are not accurately monitored and sharp peaks of pollution can be missed [18]. Although this problem can be overcome by increasing the sampling frequency over the studied period of time, the sampling procedure becomes impractical and costly [18], in addition to the impact of the applied pre-treatment method (e.g. filtration) on the apparent concentrations [18]. Many problems have been linked to filtration such as the removal of particles that are potentially mobile and may have impact on the contaminant concentrations [19]. Moreover, major difficulties are associated with the determination of groundwater contamination levels. These difficulties are related to inappropriate installation of bores (using solvent-based glue for example), replacement of the stagnant water in the borehole with fresh water (by pumping the borehole), and the use of synthetic polymers in the sampling equipment (which can sorb and desorb organic contaminants) [7]. Additionally, the samples obtained may not be representative as required due to significant loss of VOCs during sampling and handling, as well as degradation of some organic contaminants before the analysis [7]. These problems can be reduced by using on-site extraction techniques which eliminate the requirement for groundwater pumping, minimize the disturbance of the water, and increase the rapidity and the efficiency of the sampling process [7]. Fiber optic chemical sensor (FOCS) is one example of on-site measurement methods [7]. This technique depends on the measurement of the interaction between the target analyte and the light emitted by the FOCS. It is a useful method for the determination of individual contaminants; however, a single device can only be used for one target compound. Another method that does not require water pumping relies on equilibrium partitioning principles by measuring the concentrations in the vapor that is in equilibrium with the groundwater in the well followed by determination of the concentrations in the water based on Henry's coefficients; however, this method requires field-portable instruments that are

capable of detections of volatile compounds at low levels [20]. Passive sampling methods, on the other hand, are increasingly employed in water sampling for their advantages over other sampling methods as discussed in the next sections of this chapter.

Analytical methods for water sample analysis involve three major steps: extraction and preconcentration, separation, and detection. The challenge in this process, when VOCs are targeted, is to select a rapid and efficient sample preparation technique with minimal loss of the studied compounds [2]. Extracting VOCs from water samples can be achieved by static headspace (HS) extraction [21], or dynamic headspace extraction, which is referred to as purge-and-trap (P&T) [22]. In the static headspace extraction, the water sample is left at a given temperature in a sealed vial to allow vaporization of volatiles until equilibrium is reached. At equilibrium, a sample from the headspace is drawn and injected into the GC manually in a gas-tight syringe or automatically using the headspace autosampler [2]. When dynamic headspace extraction (P&T) is performed, an inert gas is purged through the sample stripping off the analytes which are subsequently trapped in a solid sorbent to be thermally desorbed and injected into the GC [2]. This technique is employed in many EPA methods, such as Method 524.3 [23]. Solid-phase microextraction (SPME) [24] and stir bar sorptive extraction (SBSE) [25] are popular methods in which the target analytes are trapped in a polymeric sorbent coated on a solid support. Other methods implemented for extracting VOCs from water include, but are not limited to, membrane inlet mass spectrometry (MIMS), which has been developed to suit on-site monitoring [26]; membrane extraction with a sorbent interface (MESI) [27]; single-drop microextraction (SDME) [28]; and liquid phase microextraction (LPME) [29]. As previously discussed, VOCs are separated after extraction using GC, and detected using MS, ECD or FID.

1.3.1.3. Sampling from bulk soil

Due to their multiphase nature, VOC measurement in soil relies on soil gas or bulk soil assessments [30]. Although rapid and economical, soil gas measurements do not reflect the total concentration of VOCs in the soil (sorbed, dissolved, vapor, and nonaqueous-phase liquids) [30]. On the other hand, the concentrations of VOCs in all phases can be measured from bulk soil samples when appropriately sealed and preserved [30]. The concern in the latter method is that VOC loss before the analysis leads to poor measurement accuracy. Proper selection of the sampling method is based on the nature of the soil: in air-filled porous soil, soil gas sampling can be a suitable method, whereas in a soil with high moisture content, high clay content, or high bulk density, bulk soil sampling would be the proper method [30].

In general, in vapor intrusion investigations, bulk soil sampling is not recommended due to the lack of correlation between the measured bulk soil concentrations and the soil gas concentrations [31]. This lack of correlation is attributable to the loss of VOCs during the collection of soil samples [31]; the dependence of the soil vapor concentration on many variables, such as moisture level, organic contents, magnitude and heterogeneity of the particle size; and variations in soil composition [32]. Nevertheless, in some cases, soil gas sample collection may not be simple according to the soil properties as previously explained. In such cases, analysis of soil headspace is expected to provide better information about vapor intrusion potential [31].

Soil samples are usually collected through a probe inserted to the required depth [30]. The samples are then treated and sealed as required for the extraction and the analytical methods selected for the desired purposes. When VOCs are extracted from bulk soil, many parameters are to be considered such as porosity, density and particle size [33]. The matrix capability of

releasing the sorbed analytes during extraction is determined to a large extent by the matrix adsorption capacity [33]. This capacity is determined by the available surface area and is dependent on the compound diffusivity, the water content, aging, and chemical and physical properties of the soil [33].

Static headspace, purge and trap (P&T), solvent extraction, and SPME are extraction techniques commonly used for VOC extraction from soil. Other techniques such as Microwave Assisted Extraction (MAE), Accelerated Solvent Extraction (ASE), and Supercritical Fluid Extraction (SFE) are also available; however, ASE and SFE are less suited for VOCs due the loss of the target analytes and the high cost of the instrumentation [33]. Static headspace extraction is the extraction method used in EPA method 5021 [34]. This method is simple in principle; nevertheless, many drawbacks are associated with it such as the difficulty to achieve the required thermodynamic equilibrium between the soil sample and its headspace and to obtain a quantitative calibration, in addition to the loss of analytes caused by heating of the sample to enhance the sensitivity of the method [33]. P&T is used in EPA method 5035 [35], in which the soil samples are placed in a hermetically-sealed vial followed by water addition and P&T extraction without opening the vial. P&T is also used in EPA method 5030 [36] after methanol extraction. The most challenging task, when VOCs are targeted, is the prevention of analyte loss during sampling, handling and transporting of the studied soil. Many on-site preservation methods (to minimize the VOC loss) have been used such as methanol, water, or sodium bisulfate solution preservation. The choice of the preservation method can be optimized based on the target analyte properties (such as Henry's constant and degradability) and the required detection limits [37]. Solvent extraction can be used in conjunction with a subsequent static or dynamic headspace extraction step [38]. Additionally, solvent extraction is used as an

independent extraction method followed by the analysis using GC and the selected detection method [33]. Methanol is a common choice for solvent extraction. It is characterized by efficient penetration into the intraparticle regions, which increases the diffusivity of the analytes allowing acceptable detection limits to be obtained [33]. In addition to being a preservative and a partitioning solvent, methanol extraction makes it possible to perform replicate analysis and dilutions from each sample [30]. Although widely applied, the solvent addition method leads to a large solvent chromatographic peak, elevating the reporting limits. Headspace SPME extraction has proven to be an effective tool for extracting VOCs from soil samples using the internally cooled SPME device. In this technique, the soil sample is heated while the fiber in the SPME device is simultaneously cooled using liquid carbon dioxide (CO_2) [39]. This method allows thermal desorption of the analytes from the soil, enhances mass transfer into the headspace, and increases the partition coefficients of the analytes by creating a temperature gap between the headspace and the fiber [39]. Finally, separation and detection after extracting VOCs using one of the above explained methods is achieved using GC-MS (EPA method 8260 [40]), GC-FID (EPA method 8015 [41]), GC- photo ionization detection (PID) (EPA method 8021 [42]), or other procedures such as GC-ECD.

1.3.2. Passive Sampling

Passive sampling, as defined by Górecki and Namieśnik, is “any sampling technique based on free flow of analyte molecules from the sampled medium to a collecting medium, as a result of a difference in chemical potential of the analyte between the two media” [43]. This gradient in the chemical potential is the overall driving force resulting from temperature, pressure, concentration, or electromotive gradients [44].

Passive sampling is an effective tool for most sample preparation goals: pre-concentration of the analytes to achieve better sensitivity of the analysis, chemical modification of the analyte's form to allow analytical measurement, and reduction of solvent consumption [43]. Additionally, not only do passive samplers provide accurate results, but they also overcome most of the active samplers' disadvantages, being of a relatively low cost, simple in design, and easy to operate with no need for power sources or attended operation [45]. Most importantly, passive samplers are capable of determining the time weighted average (TWA) concentration of the analyte [43], which is the average concentration of an analyte over a period of time [14]. In fact, the measurement of this concentration minimizes the effects of temporal variations on concentration. This measurement is problematic using active samplers due to the short sampling time, unlike that of passive sampling [43]. These advantages become more significant when sampling over a wide, remote area with multi-sample collection [45].

With different geometries and materials according to the type of the matrix and the target compounds, most passive samplers consist of a barrier and a sorbent (receiving phase) [32]. Based on the type of the barrier, two types of passive samplers are available: diffusion-type samplers, in which the barrier is a static layer of the matrix, and permeation-type samplers, in which the barrier is a polymer membrane [32]. In the latter type, the selection of the membrane material, its thickness and homogeneity determines the permeability of the barrier [46]. However, since permeation involves not only diffusion but also dissolution of the analytes into the membrane, the membrane material has a major influence on the transport of contaminants through it [46]. In both types of passive samplers the barrier defines the uptake rate of the sampler [32]. Nonetheless, the boundary layer, which is the region near the sampler in which the concentration is depleted with respect to the bulk concentration [14], may significantly influence

the mass flux into the sampler [32]. This influence occurs because the analyte transport within this layer is controlled by diffusion [47].

1.3.2.1. Non-equilibrium vs. equilibrium passive samplers

Passive samplers are designed to work in one of two accumulation regimes that determine two regions of operation (Figure 2): linear (kinetic) uptake region and equilibrium uptake region [45].

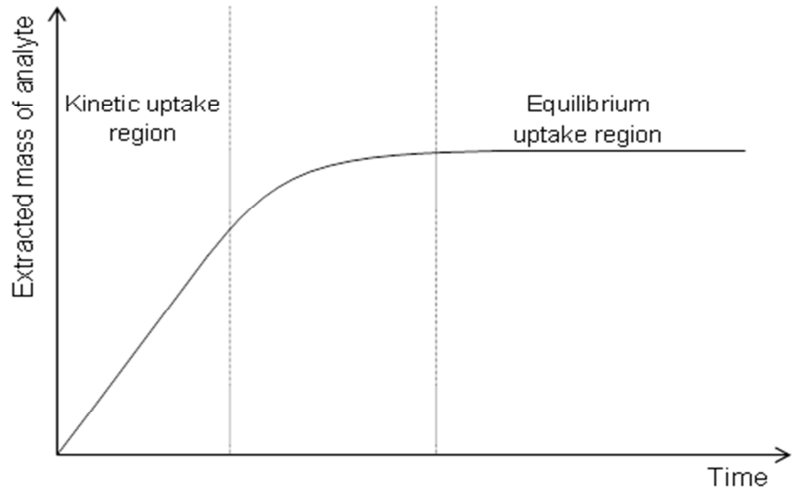

Figure 1-2- Extracted mass profile of passive samplers (based on ref. [42])

In the first region, the uptake of analytes into the sorbent is linearly proportional to the chemical potential difference between the sample and the sorbent [45]. Due to the high capacity of this type of passive samplers, the equilibrium is not reached within the sampling period [45]. It is also assumed that the uptake rate of the non-equilibrium (kinetic) sampler remains constant during the exposure time, and the mass of analytes trapped in the receiving phase is proportional to their concentration in the matrix [32, 45]. A calibration step is essential for these samplers in order to determine their uptake rates toward the analyte(s) of interest [45]. This calibration is

based on the assumption that the sampling rate is constant during the sampling period and the concentration of the analytes at the barrier-sorbent interface is zero (so-called zero sink) [45].

In the equilibrium region, the accumulation regime is controlled by the partition coefficient between the receiving phase and the matrix [45]. Samplers that work in this region achieve equilibrium between concentrations in the receiving phase and in the sampling matrix during the time of sampling [45]. Whereas the concentration obtained using this type of samplers reflects the concentration of the analyte at the time of retrieval, the concentration obtained by the kinetic uptake passive samplers reflects the TWA concentration of the analyte of interest [48].

1.3.2.2. Passive sampling from air

Many techniques are used for volatile organic compound (VOC) sampling from air. SUMMA™ canisters, Solid-Phase Microextraction (SPME) devices and the Waterloo Membrane Sampler (WMS) are examples of samplers used in monitoring VOCs in air. Other passive samplers used for sampling VOCs from air include, but are not limited to, the 3M™ Organic Vapor Monitor (OVM) 3500 sampler [14] and the Polyurethane Foam (PUF) passive sampler [49]. The SUMMA canisters and the SPME devices are introduced in the next section, while the WMS is introduced later, as it is the main focus of this work.

A SUMMA™ canister (Figure 1-3) is a treated canister which is depressurized prior to sampling in order to collect air samples based on the pressure difference between the inside of the container and the ambient air [32]. This pressure difference, which drives analyte transport into the sampler, is a form of chemical potential difference; therefore, the SUMMA™ canister still complies with the definition of passive samplers [32]. The sampling period of this device is determined based on the controllable flow rate and the volume of the canister. Although

sampling with SUMMA^{TM} canisters is a reliable technique in a wide range of applications, the cost and the complexity of sample collection and processing procedures are considerable disadvantages of this sampler [14].

Figure 1-3: SUMMA canisters (reprinted from ref. [13])

The Solid Phase Microextraction (SPME) device (Figure 1-4) is another convenient passive sampler with a significant number of applications. The SPME device consists of a fused silica fiber coated with a sorption material and protected inside a metal needle [32, 50]. Partitioning of analytes occurs when the coated polymeric stationary phase is exposed to the sampled matrix (by pressing on the plunger of the device) until equilibrium is reached [32, 50]. This technique has been effectively applied for sampling from gas, liquid, and solid matrices, and successfully coupled with gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). It has many advantages being a simple, sensitive, economical, and rapid technique, in addition to the small sample volume required and solvent elimination [50]. Fibre-retracted SPME device can also be used to measure the average concentration of the analyte of interest over a period of time (TWA concentration) [51]. Additionally, on-site applicability has been developed by coupling SPME with portable GC-MS for direct and rapid analysis [52].

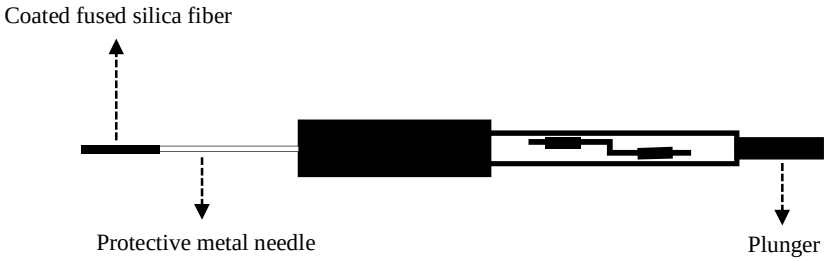

Figure 1-4: Design of the SPME device

1.3.2.3. Passive sampling from water

Passive sampling techniques are an effective tool for monitoring pollutants in aqueous matrices as in-situ collection methods that do not affect the sampled solution [18]. Semipermeable membrane devices (SPMDs) are common sampling devices that are increasingly used for sampling hydrophobic contaminants in aquatic media. They consist of lay-flat, low-density polyethylene (LDPE) tubing filled with highly pure triolein [18]. This type of sampler can provide TWA concentrations not only in water, but also in air and soil [32].

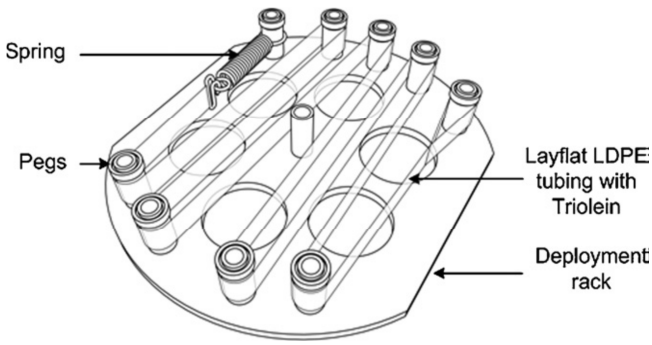

Figure 1-5: SPMD rack (reprinted from ref. [32])

The SPME device is also a common sampling device used in water sampling by either direct exposure to the aqueous sample or exposure to the headspace of the sample. A special type of SPME device with a removable needle and a gas tight syringe was developed by Ouyang et al. for in-situ TWA water sampling [53]. Thin-film microextraction (TFME), consisting of a thin

film of PDMS mounted on a stainless steel wire, is also an extraction technique that has been used for extracting organic contaminants from water, mainly for on-site sampling [54]. Due to the high surface area to volume ratio of this device, the equilibrium time is shorter and the extraction rate is higher than for the coated fiber [54]. TFME can also be used for measuring the TWA concentrations of the analyte in the studied water [54].

Vapor intrusion investigations often involve groundwater sampling, although it is considered a secondary line of evidence because groundwater is generally the farthest of all media involved in vapor intrusion to indoor air [31]. However, due to data availability, existing protocol development, and transport predictability, groundwater sampling is a desirable line of evidence for evaluating potential impact over large areas [31]. Also, groundwater sampling is the main line of evidence when the water table is at a depth similar to the basement depth [31].

As a no-purge sampling technique, passive sampling, both equilibrium and kinetic, is widely employed in groundwater sampling to monitor VOC contamination. In addition to all previously explained passive sampling advantages, the loss of VOCs during transport and storage of samples is minimized in passive sampling techniques once analytes are trapped in the sorption phase [55]. Also, depth-specific samples are desirable for certain applications [56].

In general, a receptacle of a semipermeable or permeable membrane is the main component of equilibrium-type passive samplers that are used for groundwater sampling [56]. This membrane contains analyte-free vapor or water, which leads to mass transfer of VOCs from the contaminated water (matrix) to the water or air in the sampler until equilibrium is achieved [56]. An example of this type of samplers is the Polyethylene Diffusion Bag (PDB) [18].

Amongst the kinetic passive samplers, the ceramic dosimeter is a representative example that is capable of long term monitoring [56]. This sampler consists of a water-saturated adsorbent enclosed in a ceramic tube with caps made of polytetrafluoroethylene (or a similar material) at both ends [57]. The effect of the boundary layer thickness is decreased by the thickness of the sampler's wall [57]. However, the thickness of the wall leads to a lower diffusion rate, which means that rapid contamination peaks may not be observed [57].

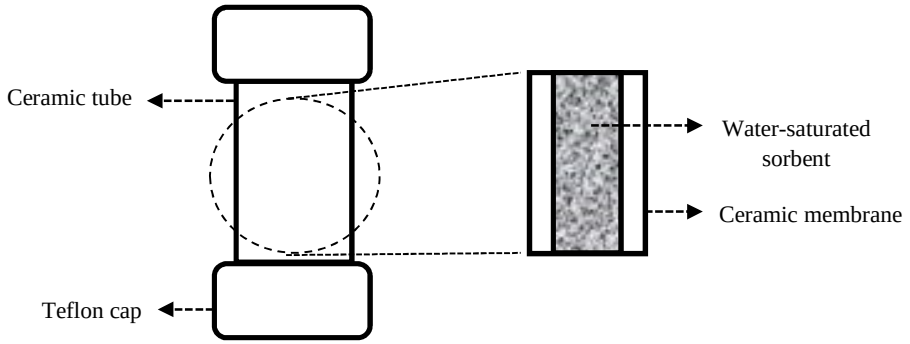

Figure 1-6: Design of the ceramic dosimeter

1.3.2.4. Passive sampling from soil

Soil gas sampling is the core of passive sampling from soil [32]. In this method, the passive sampler is deployed underground to be retrieved later for analysis [31]. Passive samplers have shown sensitivity and capability of collecting volatile compounds from the vapor in soil pores with less susceptibility to changes in subsurface or ambient conditions than other sampling techniques [58]. Moreover, relative subsurface VOC concentrations can be mapped by passive sampling [31], while the natural vapor equilibrium in the subsurface is not disturbed by sample collection.

The GORE^{TM} sampler (Figure 1-7) is one of the most commonly used passive samplers in soil gas sampling. It consists of several units of sorbent materials that are selected to adsorb a

wide range of volatile and semi-volatile organic compounds [58]. The sorbers are protected from soil particles and water by a microporous hydrophobic membrane (GORE-TEX) [58].

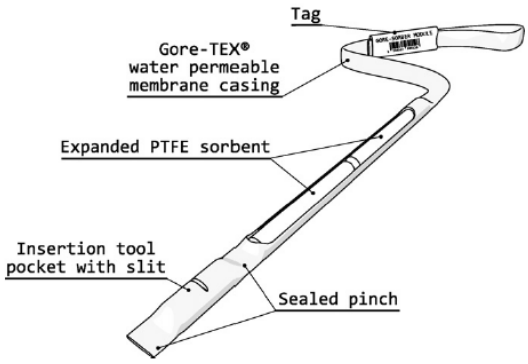

Figure 1-7: Design of the GORE Sampler (reprinted from ref. [59])

The PETREX passive sampler is another passive sampling tool used in monitoring VOCs and semi VOCs (SVOCs) in soil gas and sediment vapor [59]. This sampler consists of two or three adsorption components of activated carbon fused to a ferromagnetic wire inside a glass tube [59]. The sampler is unsealed and exposed to the soil gas with the open end down at the bottom of a shallow borehole for a period of time sufficient to reach equilibrium [59].

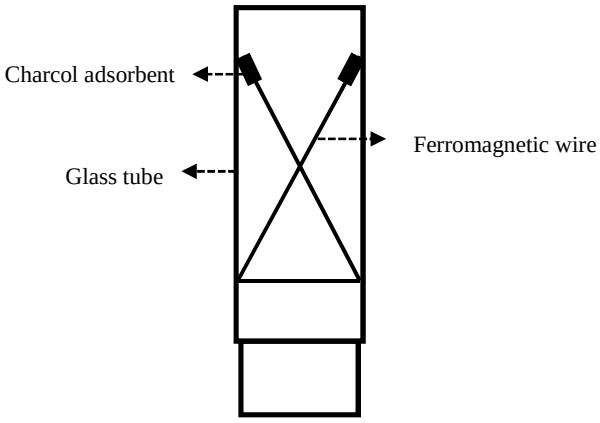

Figure 1-8: Design of PETREX sampler (based on ref. [14, 59])

1.4. Waterloo Membrane Sampler

The Waterloo Membrane Sampler is a polydimethylsiloxane (PDMS)-based permeation kinetic passive sampler developed by Suresh Seethapathy and Tadeusz Górecki at the University of Waterloo. This sampler, shown in Figure 2, consists of a glass vial with an adsorbent medium, which can be Anasorb 747 (available from SKC Inc. in 100 g quantities) or Carbopack B (available from Sigma in 10 g quantities) according to the application. A thin PDMS membrane covers the mouth of the vial, and a crimped aluminum cap holds the membrane in place [14].

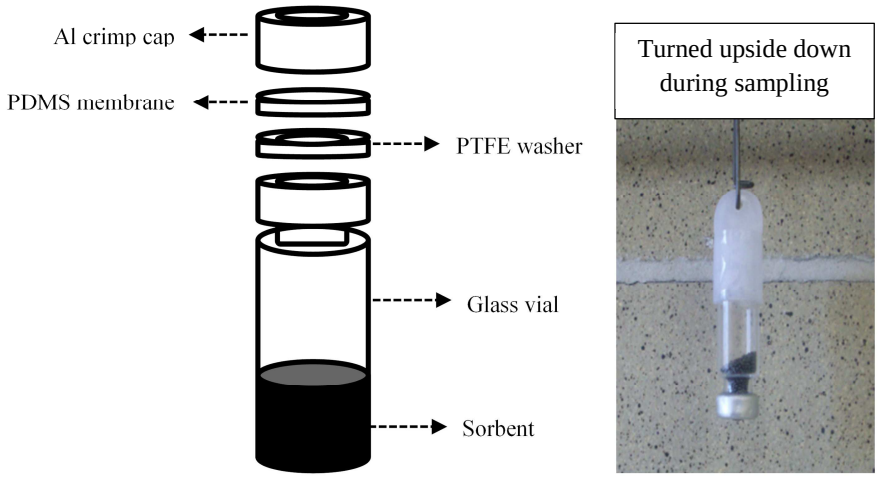

Figure 1-9: The Waterloo Membrane Sampler (WMS)

1.4.1. Description of the sampling and quantification process

The WMS is provided in a sealed, clean package. It is exposed to the sampled matrix (with the membrane facing down) for a specific exposure time (*t*). During the time of exposure,

chemicals permeate through the membrane to be trapped in the sorbent. Afterwards, the sampler is repackaged, sealed and returned to the laboratory for quantification [60].

The TWA concentration (C_0) of each analyte in the matrix is calculated (after determining its mass (M) trapped by the sorbent) as follows [14]:

$$C_0 = \frac{kM}{t} \qquad (1.1)$$

where k is the calibration constant of the sampler towards an analyte. This equation was derived from Fick's first law, according to which the mass of the analyte M (kg) collected during the time of exposure t (min) is calculated as follows [14]:

$$\frac{M}{t} = D\frac{A}{L_m}(C_{ma} - C_{ms}) \qquad (1.2)$$

where D is the diffusion coefficient of the analyte in the PDMS membrane (cm^2/min), A is the area of exposed surface of the membrane (cm^2), L_m is the thickness of the membrane (cm), C_{ma} is the analyte concentration at the air-membrane interface (kg/cm^3), and C_{ms} is the analyte concentration at the membrane-sorbent interface. Since the sorbent is assumed to be acting as a zero sink, C_{ms} is approximately zero. Also, the concentration at the air-membrane interface at a given temperature is given by eq. (1.3):

$$C_{ma} = KC_0 \qquad (1.3)$$

In this equation, K is the partition coefficient of the analyte between air and the PDMS membrane, and C_0 is the concentration of the analyte in the air.

At a constant temperature, D, K, L_m, and A are constants, so one can write

$$k = \frac{L_m}{DKA} \qquad (1.4)$$

in which k is the calibration constant of the WMS towards the analyte of interest. By substituting eq. (1.3) and (1.4) in eq. (1.2), one gets eq. (1.1). According to eq. (1.4), the calibration constant k for such a type of sampler can be controlled by adjusting the area or the thickness of the membrane [14]. The calibration constant is also dependent on the permeability coefficient of the membrane, P, which is calculated from eq. (1.5) [14]:

$$P = DK \qquad (1.5)$$

Finally, the inverse of the calibration constant k^{-1}(mL/min) is known as the uptake rate of the sampler towards the analyte [14].

1.4.2. Advantages and limitations of the WMS

Advantages

The Waterloo Membrane Sampler is fabricated and deployed for sampling with very little training required, especially when used for air sampling. Even when used for other sampling purposes like soil gas sampling, the procedure is significantly simpler and less expensive than other conventional sampling methods like SUMMA^{TM} canisters. For these reasons, in addition to the low cost of the materials involved in the fabrication (a small vial, a PDMS membrane, and a sorbent), the WMS is an economical device, especially when multiple samples are required. Additionally, the long term sampling that may extend over several weeks allows measurement of the TWA concentration, and the small size of this sampler makes it less obtrusive than other samplers commonly employed in passive sampling.

Limitations

The first concern about WMS applications is the starvation effect. This effect occurs when the analytes are trapped in the sampler faster than they are supplied into the sampler-matrix interface, which leads to depletion of the analytes near this interface. As a result, the measured concentrations do not reflect the actual concentrations in the sampled matrix [14, 60]. The starvation effect becomes more pronounced as the flow velocity around the sampler decreases, which is the case in soil gas sampling, especially in soils of low permeability [60]. Controlling the uptake rate of the WMS is a subject of current studies seeking minimization of the starvation effect. Another limitation of such type of samplers is saturation of the adsorbent phase, which may occur when the sampler is exposed to high analyte concentrations for prolonged periods [60]. Such an effect leads to a decrease in the uptake rate of the sampler toward analytes, or the replacement of weakly adsorbed compounds with strongly adsorbed compounds [60]. In order to avoid such effects, it is advisable to seek an additional source of information about the expected analyte concentration and determine the proper exposure period [60]. Finally, unplanned uptake of contaminants during storage or shipment of the sampler is one limitation that can be monitored by using trip blanks that travel and are stored with the samplers [60].

1.4.3. Previous work

In his thesis [14], Suresh Seethapathy studied the application of the WMS in air and soil gas sampling. He also measured the uptake rates of the standard air sampler towards 40 compounds from different groups using a special setup, which will be described later. Seethapathy described theoretically and demonstrated experimentally the proportionality between the natural logarithm of the uptake rate of an analyte and the linear temperature programmed retention index (LTPRI) of the analyte in a PDMS-coated GC column as a way of

estimating the uptake rate when no reliable value of the uptake rate is available, as shown in eq. (1.6):

$$\ln k = N(LTPRI) + Q \qquad (1.6)$$

where *N* and *Q* are constants. Through this correlation, a key feature of using PDMS as a barrier in the WMS was demonstrated, namely the possibility of estimating the uptake rates of unknown compounds from the LTPRI measured for the compound in gas chromatography columns with a PDMS stationary phase.

Furthermore, Seethapathy examined the effects of environmental variables on the uptake rate of the WMS. It was found that the uptake rate was affected negligibly by humidity, which is a significant advantage. Also, Seethapathy demonstrated a decrease in the uptake rate of the sampler as the temperature increased. Linear flow velocity is another essential environmental factor that influences the operation of the WMS. It was shown by Seethapathy that the uptake rates of the sampler toward analytes increased with increasing linear flow velocity until a plateau was reached (as previously explained when introducing the starvation effect). One important focus of Seethapathy's work was the determination of the effect of the WMS geometry (thickness and membrane area) on its uptake rates toward analytes. Accordingly, increasing the membrane thickness or decreasing the area of the barrier have both been shown to decrease the uptake rates. This can be employed in order to control the mass transfer rate of analytes into the sampler for different sampling purposes.

1.5. Research Objectives

1.5.1. Calibration of a modified low uptake rate version of the WMS

The first objective of this work was to determine experimentally the uptake rates of a modified low uptake version of the WMS toward different analytes when sampling from air. This study was based on the work completed by Seethapathy and aimed at providing reliable uptake rate values for a broad range of compounds that are considered sources of concern in vapor intrusion guidance documents. The sampler used in this study was of 1 mL volume and 0.113 cm^2 exposed membrane area, which was smaller than the regular sampler (2 mL volume and 0.238 cm^2 exposed membrane area). The purpose of using the smaller permeation area was to reduce the uptake rate in order to reduce the starvation effect.

1.5.2. Application of the WMS in VOC sampling from water

Another objective was to study the applicability of the WMS for sampling from water, mainly from groundwater. Although many advanced sampling methods have been developed for groundwater sampling, monitoring contaminant transport through all media involved in the vapor intrusion process using the same type of sampler would be extremely valuable. Moreover, PDMS is an ideal material for applications in water sampling because of its hydrophobicity and low permeability toward water compared to its permeability toward VOCs [61, 62]. It was also demonstrated in previous work completed by Seethapathy that the WMS uptake rates from air are not affected by humidity. Similarly, the WMS was expected to show capability of sampling from water with stable uptake rates throughout the period of exposure. To verify this hypothesis, the uptake rates of the sampler were evaluated at different concentration levels and for different exposure times. A theory was established and assessed to study the correlation between the uptake rates of the sampler in air sampling and in water sampling. The study evaluated the

WMS performance in sampling seven VOCs: 1,1-dichloroethylene, chloroform, benzene, trichloroethylene, toluene, ethylbenzene, and *o*-xylene.

1.5.3. Application of the WMS in VOC sampling from bulk soil

A new method for bulk soil sampling using the WMS was evaluated in this work. In this method, the soil sample was placed in a container along with the Waterloo Membrane Sampler in the soil headspace. The vaporized analytes were adsorbed by the sampler during the period of exposure, which was estimated to be similar to the holding time of the soil samples in conventional sampling and analysis methods. The WMS was expected to perform exhaustive extraction, i.e. extraction of the entire amount of the VOCs present in the soil sample. The concentrations of the analytes were then calculated by dividing the adsorbed mass of each analyte by the dried mass of the soil sample. Although the desired extraction was a challenging task since the soil matrix has high adsorptive capacity [63], the high adsorptivity of the carbon-based sorbent used in the WMS was expected to overcome this difficulty. Further, the effects of the exposure time, temperature, and water content on the extraction efficiency were examined.

Many advantages are obtained in this method: first, the loss of VOCs during sampling, shipping, and handling is minimized with no need for field extraction. Another important potential advantage of this method is the possibility of sampling a considerably larger amount of soil than the amount sampled in other methods (2 grams in EPA Method 5021 and 5 grams in EPA Method 5035). As a result, the acquired data is expected to be less vulnerable to small-scale variations in organic carbon fraction, which affect the VOC concentrations in the bulk soil. The focus in this work was on chlorinated VOCs, namely trichloroethylene and tetrachloroethylene,

and the starting point of the experimental procedure was the simplest scenario, which was sandy soil sampling using the method explained above.

2. CHAPTER TWO: EXPERIMENTAL CALIBRATION OF A MODIFIED VERSION OF THE WMS

A modified version of the WMS was developed by decreasing the exposed area of the membrane. The purpose of this modification was to lower the uptake rates of the sampler so that the starvation effect is minimized. In this chapter, this version of the WMS was calibrated towards 17 VOCs that were listed in the vapor intrusion documents as hazardous chemicals. The experiments were based on a procedure established by Suresh Sethapathy in his Ph. D. thesis [14].

2.1. Experimental

2.1.1. Fabrication of the WMS

The WMS calibrated in this work was prepared using a 1 ml glass vial with 150 mg of Anasorb 747® enclosed. Anasorb 747® is an activated carbon-based sorbent described by the manufacturer as "a synthetic carbon with low ash content" and available from SKC Inc. in 100 g quantities. A PDMS membrane, fabricated in our laboratory as described in the next section, was cut to fit the top of the vial using a die of a matching size and was held in place with an aluminum crimped cap. The thickness of the membrane used in this thesis was approximately 80 µm, and it was controlled by weighing the membranes (the area cut by the die was constant). In this application, the desired weight of the membrane was 3.7±0.2 mg. Since the thickness of the membrane is smaller than the thickness of the septum of the crimp cap, a PTEF washer was placed between the mouth of the vial and the PDMS membrane. The washers used in this part of the research were natural PTFE washers of the dimensions: 0.040" x 0.281" x 0.188" (thickness x OD x ID), purchased from Penn Fibre Plastics.

2.1.1.1. Preparation of the PDMS membrane

A mixture of silicone elastomer base and silicone elastomer curing agent (10:1) was mixed for half an hour. These components are available as SYLGARD® 184 SILICONE ELASTOMER KIT from Dow Corning, USA. The mixture was placed afterwards under vacuum inside a closed vacuum manifold for another half an hour with intermittent releasing of the air to remove the bubbles. The mixture was then coated on the surfaces of polished crystalline silicon wafers of 19.95 cm diameter (part no. 6TPP1051, from MEMC KOREA COMPANY). Approximately 10 g of the mixture was placed on the center of the wafer to be processed in a precision spin coating machine (Cee® model 200X, available from Brewer Science, Inc). In the coating method designed for the desired membrane thickness (~ 80 µm), the wafers were processed for 60 s at the velocity of 625 RPM with a 500 RPM/s ramp. The coated wafers were then left at 60 °C for two hours. After cooling the membranes to room temperature, they were coated with fumed silica powder (Catalogue no. S5505, purchased from Sigma-Aldrich, Canada, available in 100 g quantities) before they were peeled off and used. The purpose of coating the membrane with silica powder was to prevent the sorbent material inside the WMS from sticking to the membrane, which leads to difficulties with recovering all the sorbent.

2.1.2. Solvents and chemicals

High purity carbon disulfide (CS_2), used as a solvent for all the calibration standards and as an extraction reagent for desorbing analytes from the sorbent (Anasorb 747), was purchased from Sigma-Aldrich, Canada. All chemicals were of analytical grade, purchased from Sigma-Aldrich, Canada, as well. High purity helium gas, used as the mobile phase in gas chromatography, was procured from Praxair (Kitchener, ON).

2.1.3. The experimental setup for uptake rate measurement in air sampling

Suresh Seethapathy designed the setup shown in Figure 2-1 to expose the Waterloo Membrane Samplers to an atmosphere of analytes with measurable concentrations for a specific period of time [14].

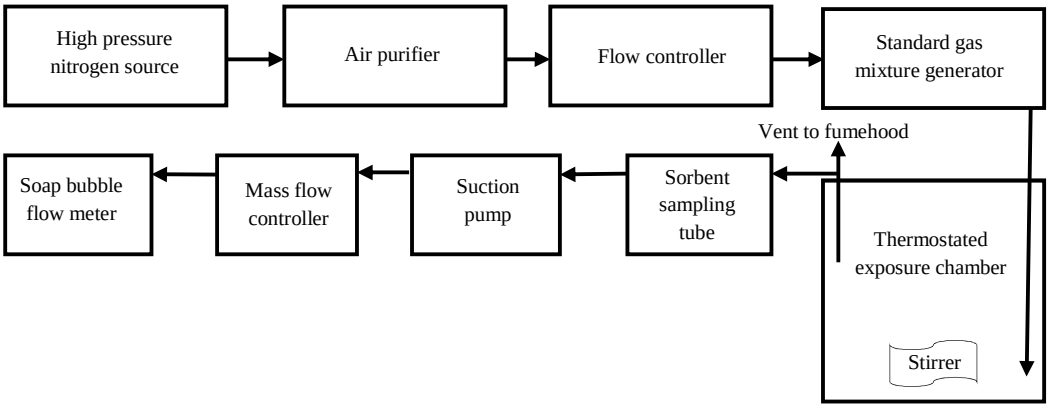

Figure 2-1: Experimental setup for calibration constant measurement in air sampling (based on ref. [14])

The function of each component of the setup shown in Figure 2-1 can be explained as follows [14]: after passing through the air purifier, which trapped traces of VOC contaminants, nitrogen entered the standard gas mixture generator at a flow rate controlled by a mass flow controller (model MDF-52000L0N-0L) obtained from Pneucleus Technologies Inc., (Hollis, NH). The operating range of the mass flow controller was 0 to 1000 mL/min. An MKS 4-channel readout system (Andover, MA, Type 247) was connected in series to the mass flow controller to set and monitor the flow. In this study, the flow rate was set at 800 mL/min. The standard gas mixture was generated using polytetrafluoroethylene (PTFE) permeation tubes in which a neat liquid analyte was enclosed (Figure 2-2). The permeation tubes were ordered from Virgin PTFE Tubing. The outer diameter of the tubes was ¼" and their wall thickness was 290 μm. They were cut into pieces of the desired length (~ 17.5 cm in this work). The tubes were sealed from

both sides using PTFE plugs, which were produced from 1/4" PTFE rods by reducing their diameters to tightly fit the openings of the tubes. ¼" brass Swagelok® ferrules were tightened from both sides to seal the ends of the tubes against the PTFE plugs.

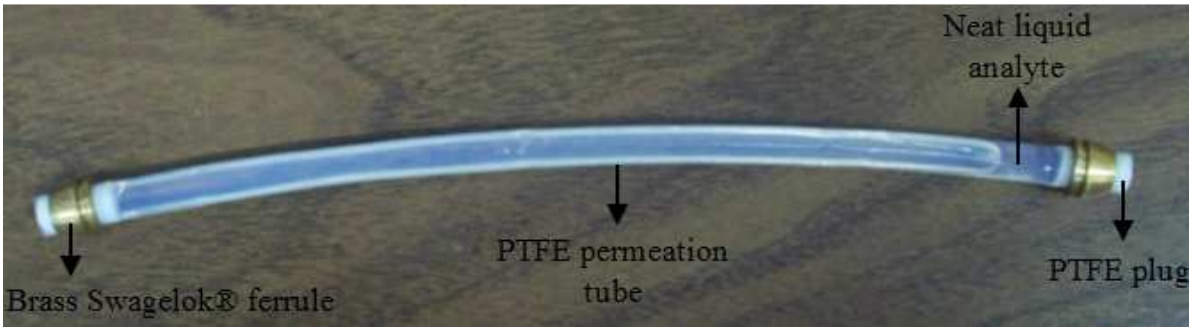

Figure 2-2: A permeation tube used for standard gas generation

The liquid inside the permeation tube permeated through the PTFE walls to be swept by the purified nitrogen and enter the calibration chamber. The flow-through vessel, in which the permeation tubes were enclosed, was kept at a constant temperature inside a GC oven. The temperature inside the oven was adjusted based on the desired permeation rate of the studied compounds. The calibration chamber (Figure 2-3) consisted of a 10 L cylindrical glass jar with a PTFE plate on top. The PTFE plate was sealed against the jar walls with a PTFE-encapsulated Viton O-ring. Two aluminum plates were used to hold the chamber's parts together: one on top of the PTFE cover and another below the jar and the thermostated jacket. The two plates were fixed in place using stainless steel threaded rods with tightened nuts on the top ends. The glass chamber was wrapped with an isolated thermostated jacket through which a radiator fluid was circulated by means of a circulation thermostat (VWR Programmable Temperature Controller-model 1147P). The temperature at which the samplers were exposed in all experiments performed in this part was 25 ºC. In order to keep uniform concentrations inside the chamber, a circulation fan, made of high-density polyethylene, was enclosed inside the chamber and connected to a motor on top (model JB2PO21N, Universal Electric Company, MI). The motor's

circulation speed was controlled by means of a Powerstat® variable autotransformer (Type 3PN116B, Superior Electric Company, CT). The standard gas entered the chamber through a copper tubing inlet of ¼" diameter inserted through the top plates. The passive samplers were exposed through eight holes in the top plates of the chamber. Concentrations of the analytes inside the chamber were measured using a sorption tube (active sampling) through which a sample from the atmosphere inside the calibration chamber was drawn by means of a suction pump (Model MB-21). The flow rate through the sorption tube was controlled by an MKS mass flow controller (1179A53CS1BV Gas: N2 Range: 5000 SCCM) (not included in Seethapathy's setup) and measured with a bubble flow meter. The sorption tubes used in this work were stainless steel tubes of 89 mm length and 6.42 mm outer diameter procured from Perkin Elmer. 250 mg of Anasorb 747 was packed inside the sorption tube between the mesh and a glass wool layer. The flow rate through the sorption tube during active sampling was controlled at 79 ml/min, and the sampling time varied between 30 min and 90 min depending on the concentration inside the chamber and the analysis sensitivity towards the target analyte.

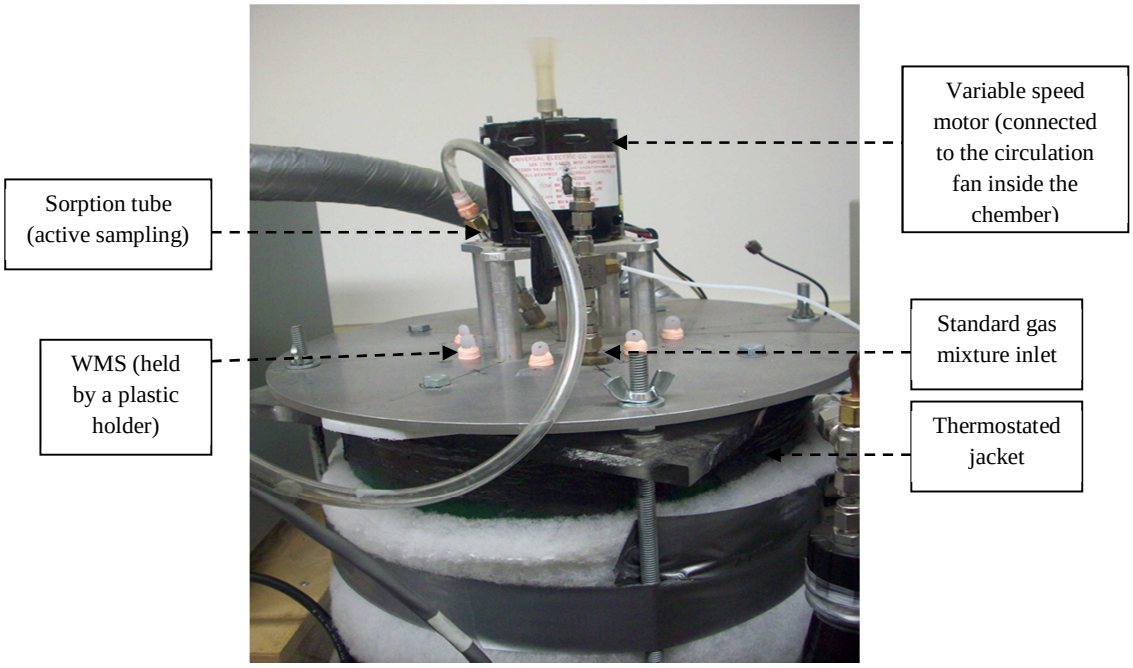

Figure 2-3: The calibration chamber used for the calibration of the WMS in air sampling

2.1.4. Desorption of analytes

The sorbent used in both active sampling (sorption tubes) and passive sampling (WMS) was transferred after sampling into 4 ml glass vials with PTFE/SIL screw caps. One ml of CS_2 (the desorbing solvent) was added to the vial, which was subsequently sealed and left for 40 min at ambient temperature with intermittent shaking. Aliquots from the extract were then transferred to 2 ml crimp top chromatographic vials with 100 µl glass inserts (available from Chromatographic Specialties Inc.) for analysis.

2.1.5. GC-MS instrument

Analysis was performed using an Agilent 6890 GC- 5973 MS system equipped with a 7683 Agilent autosampler with a tray of a 100-sample capacity and a Hewlett Packard (*hp*) 3683 injector. An Rxi-1 MS capillary column (60 m x 0.32 mm ID x 1.0 µm film thickness) was used

with helium as the carrier gas. Data acquisition and processing were done using Chemstation software.

2.1.6. GC-MS method

The injection was performed in split mode at 1:10 split ratio and 250 ºC inlet temperature. The carrier gas flow rate was set at 2 ml/min, and the injection volume was 2 µl. The oven temperature program was set as follows: 35 ºC for 5 min, a ramp of 5 ºC/min up to 120 ºC, and a second ramp of 30 ºC/min up to 300 ºC which was held for 2 min. External standards were used for multipoint calibration. Selected Ion Monitoring (SIM) mode was used with 2-3 ions for each compound as shown in Table 2-1.

Table 2-1: Ions used for the analysis of the compounds in MS SIM mode

Compound	Ions used in the SIM mode (m/z)
1,1-Dichloroethane	63, 83, 98
1,1,2-Trichloroethane	97, 83, 61
1,2-Dichlorobenzene	146, 111
Cumene	105,120, 77
1,2,4-Trichlorobenzene	182, 145, 109
m-Xylene	91, 106, 77
Chloroform	83, 85
Chlorobenzene	112, 77
P-Xylene	91, 106
1,1,1,2-Tetrachloroethane	131, 117, 95
1,1,2,2-Tetrachloroethane	83, 85, 95
1,2,3-Trichloropropane	75, 77, 61
Acrylonitrile	53, 52, 51
1,2-Dichloropropane	63, 62, 76
Dibromochloromethane	129, 127, 131
1,2-Dibromoethane	107, 109, 81
1,4-Dichlorobenzene	146, 111, 75

2.2. Results and discussion

The concentration of an analyte inside the exposure chamber was calculated, after determining the mass collected by the sorption tube, by dividing the mass of the analyte by the air volume passed through the tube during the sampling time. By knowing the concentration inside the chamber, the mass of the analyte collected by the WMS, as well as the exposure period (1 to 2 days in this work), the calibration constant was calculated for each analyte using eq. (1.1).

The first set of compounds included 1,1-dichloroethane; 1,1,2-trichloroethane; m-xylene; cumene; 1,2-dichlorobenzene; and 1,2,4-trichlorobenzene. Calibration of the WMS towards these compounds was done in four experiments at different exposure times with the permeation tubes of these compounds kept at 40 ºC. ANOVA test (Analysis of Variances) was used to verify that the exposure time has no significant effect on the calibration constant values. The results, presented in Table 2-2, demonstrate high reproducibility between the samplers in each experiment and reasonable reproducibility between calibration constant averages obtained from different experiments (RSD values up to 25% were considered acceptable throughout this thesis). Comparing F statistical value, acquired from ANOVA test for one factor at 5% significance level, with the critical F value, it can be concluded that the exposure time did not show significant effect on the uptake rates of the sampler towards the studied analytes (F_{Stat} was smaller than $F_{Critical}$).

The other compounds were studied in three sets: chloroform, chlorobenzene, and p-xylene (permeation tubes kept at 40 ºC); 1,1,1,2-tetrachloroethane, 1,1,2,2-tetrachloroethane, and 1,2,3-trichloropropane (permeation tubes kept at 50 ºC); and acrylonitrile, 1,2-dichloropropane; dibromochloromethane; 1,2-dibromoethane, and 1,4-dichlorobenzene (permeation tubes kept at 30 ºC). Each set of compounds was studied in two experiments at two different exposure times.

High reproducibility between samplers and experiments was achieved for all compounds as demonstrated in Table 2-3. Student's t-test for two samples assuming equal variances at 5% significance level indicated that there were no statistically significant differences between the results obtained in both experiments (t_{Stat} smaller than $t_{Critical}$).

Table 2-2: Calibration constants, obtained from four experiments at different exposure times, for six VOCs

Compound	Exposure time (min)	Concentration (g/m3)	k (min/ml)	n	RSD (%)	k (ave) (min/ml)	RSD (%)	F	F crit	P-value
1,1-Dichloroethane	6123	1.77E-03	2.46	7	3.5	2.20	9.5	5.311	5.987	0.061
	2929	1.75E-03	2.12	8	8.1					
	1478	1.84E-03	2.26	7	3.5					
	624	1.69E-03	1.97	8	2.8					
1,1,2-Trichloroethane	6123	4.71E-04	0.57	7	5.0	0.50	11.0	5.318	5.987	0.061
	2929	6.00E-04	0.46	8	5.4					
	1478	6.36E-04	0.50	7	1.1					
	624	4.28E-04	0.46	8	4.4					
1,2-Dichlorobenzene	6123	1.48E-04	0.13	7	7.5	0.11	12.6	5.319	5.987	0.061
	2929	1.95E-04	0.10	8	7.2					
	1478	2.00E-04	0.12	7	3.8					
	624	1.34E-04	0.10	8	6.7					
Cumene	6123	9.47E-05	0.34	7	8.1	0.28	17.4	5.318	5.987	0.061
	2929	1.26E-04	0.23	8	6.1					
	1478	1.28E-04	0.26	7	1.9					
	624	8.04E-05	0.27	8	8.9					
1,2,4-Trichlorobenzene	6123	1.05E-04	0.08	7	8.6	0.07	14.1	5.319	5.987	0.061
	2929	1.72E-04	0.06	8	8.6					
	1478	1.76E-04	0.08	7	5.3					
	624	9.23E-05	0.06	8	7.5					
m-Xylene	6123	3.94E-04	0.31	7	6.3	0.28	11.5	5.318	5.987	0.061
	2929	4.47E-04	0.24	8	5.7					
	1478	4.70E-04	0.27	7	1.9					
	624	3.51E-04	0.28	8	8.1					

Table 2-2: Calibration constants, obtained from two experiments at different exposure times, for 11 VOCs

Compound	Exposure time (min)	Concentration (g/m3)	k (min/ml)	n	RSD (%)	k (ave) (min/ml)	t_{Stat}	$t_{Critical}$ (2-tail)	P-value (2-tail)
Chloroform	1524	1.02E-03	1.93	7	7.5	1.91	0.474	2.228	0.646
	2862	1.02E-03	1.90	5	3.2				
Chlorobenzene	1524	3.59E-04	0.43	7	5.2	0.42	0.958	2.228	0.361
	2862	3.39E-04	0.42	5	2.3				
p-Xylene	1524	2.96E-04	0.41	7	5.2	0.41	-0.828	2.228	0.427
	2862	2.81E-04	0.41	5	3.5				
1,1,1,2-Tetrachloroethane	1423	2.19E-04	0.29	7	7.1	0.29	1.097	2.179	0.294
	2879	1.95E-04	0.28	7	11.8				
1,1,2,2-Tetrachloroethane	1423	1.28E-04	0.13	7	8.9	0.13	-0.903	2.179	0.384
	2879	1.59E-04	0.13	7	9.8				
1,2,3-Trichloropropane	1423	9.57E-05	0.16	7	7.0	0.16	-1.174	2.179	0.263
	2879	8.78E-05	0.17	7	10.3				
Acrylonitrile	2936	1.97E-03	1.60	8	3.4	1.59	0.471	2.145	0.645
	1423	1.65E-03	1.57	8	10.4				
1,2-Dichloropropane	2936	3.18E-04	0.96	8	3.3	0.96	-0.215	2.145	0.833
	1423	2.74E-04	0.96	8	4.3				
Dibromochloromethane	2936	2.72E-04	0.42	8	4.9	0.42	0.708	2.145	0.490
	1423	2.25E-04	0.41	8	3.0				
1,2-Dibromoethane	2936	5.03E-04	0.30	8	5.8	0.31	-0.971	2.145	0.348
	1423	4.10E-04	0.31	8	4.3				
1,4-Dichlorobenzene	2936	1.84E-04	0.10	8	6.8	0.10	0.824	2.145	0.424
	1423	1.46E-04	0.10	8	3.1				

2.2.1. Conclusions and recommendations

A modified low uptake version of the WMS was calibrated towards 17 VOCs. The calibration constant values obtained from several experiments demonstrated reproducibility at different exposure times. ANOVA test, used to examine the effect of the exposure time on the uptake rates of the sampler, showed insignificant effect of this factor, meaning that the uptake rate is independent of the exposure time within the studied exposure periods. Further experiments are recommended to determine the uptake rates of this sampler toward an expanded range of VOCs. It is also recommended to examine the linear range of the sampler uptake over a longer exposure time.

3. CHAPTER THREE: ASSESSMENT OF WMS APPLICABILITY IN SAMPLING FROM WATER

The WMS was expected to be capable of VOC sampling from water due to the hydrophobicity of the PDMS membrane and its low permeability toward water compared to its permeability toward VOCs. In this chapter, the performance of the WMS in sampling from water was examined. Experiments were designed to expose the sampler to an aqueous solution of the studied analytes with concentrations determined using SPME as a reference method. The uptake rate values of the sampler were experimentally determined and compared at different concentration levels and for different sampling periods. A hypothesis was established to theoretically calculate the calibration constant value in water sampling based on its value in air sampling. This hypothesis was evaluated by comparing the experimental results of the calibration constant measurement in sampling from water with those calculated based on the theory.

3.1. Experimental

3.1.1. Fabrication of the WMS

A 2 ml glass vial with 250 mg of Anasorb 747® was used for WMS fabrication in this application. As described in Section (2.1.1), a PDMS membrane was cut using a die of the same cutting area as the top of the vial. The membrane was held in place (at the vial opening) with an aluminum crimp cap with a PTFE washer between the vial and the membrane. The target weight of the membrane in this application was 8.0±0.5 mg. The PTEF washers used in this part (0.040" x 0.440" x 0.216"; thickness x OD x ID) were purchased from Penn Fibre Plastics.

3.1.2. Chemicals and instruments

All chemicals were obtained as described in Section (2.1.2). Highly pure methanol (HPLC grade), used for the spiking solution and for the SPME calibration standards, was obtained from Sigma-Aldrich Canada. The GC-MS system described in Section (2.1.5) was used in this part. The GC-MS method described in Section (2.1.6) was used with inlet split ratio 30:1. The ions used for the analysis in the MS-SIM mode are presented in Table 3-1.

Table 3-1: Ions used for the analysis of the samples, obtained from water exposure, in the MS SIM mode

Compound	Ions used in the SIM mode (m/z)
1,1-Dichloroethylene (1,1-DCE)	61,96
Chloroform	83,85
Benzene	78
Trichloroethylene	95,130
Toluene	91,65
Ethylbenzene	91,106
o-Xylene	91, 106

3.1.3. Experimental setup used for sampling from water

The experimental setup used for studying the applicability of the WMS in sampling from water is schematically presented in Figure 3-1.

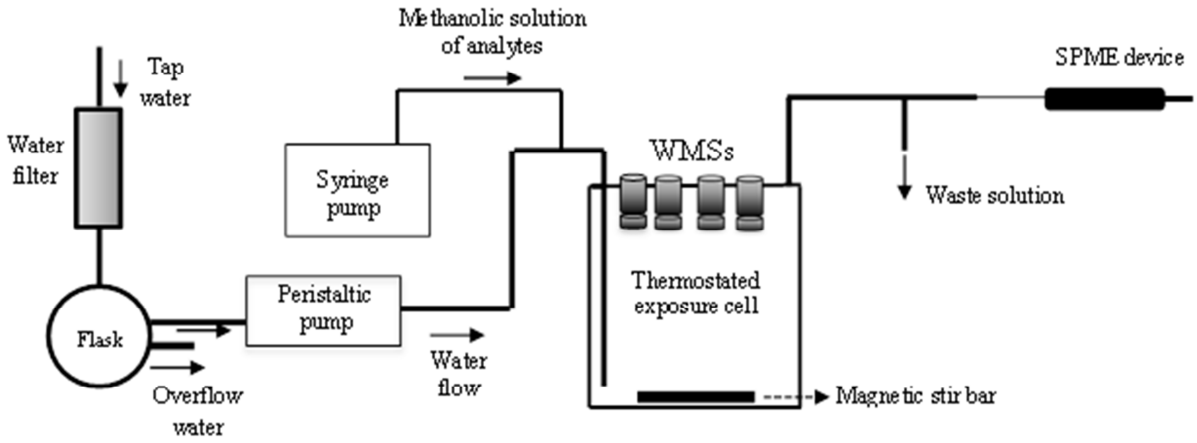

Figure 3-1: Experimental setup for water exposure

In this setup, a flow-through system was created to eliminate uncertainties caused by analyte loss by sorption onto exposed surfaces or volatilization. The function of each component of this system can be explained as follows: tap water was passed through a water filter (GXULQ, available from General Electric Appliances) to trap any dissolved VOCs. The water was then directed to a 3-neck, round-bottom flask with the water entering through a ¼" plastic tube inserted through the stopper in one neck. The flask was fixed in a position allowing overflow water to flow into the sink through a rubber tube. The water was pumped out of the flask, through a rubber tubing, by means of a peristaltic pump (OMEGA® FPU405 with 1/8"x 3/8" Norprene® tube), at ~ 46 ml/min flow rate. The analyte solution in methanol was pumped by means of a syringe pump (Single Syringe Programmable Pump, NE-1000, equipped with a 10 ml, gas-tight SGE Analytical Science Syringe, all purchased from Bio-Lynx Science Equipment Inc.) at a low flow rate (0.1 $ml.h^{-1}$) to keep a negligible concentration of methanol in the aqueous solution. The methanolic spiking solution was pumped through a 1/8" stainless steel tube to be mixed with the water inside a stainless steel union tee which was attached to a 1/4" stainless steel tubing inserted through the top plate and extended nearly to the bottom of the exposure jar. A custom-made glass container of 1.15 L capacity was used as an exposure cell (Figure 3-2). The jar was provided with a thermostated water bath controlled by a circulation thermostat (HAAKE, type: FJ, NR: 72 1259) to keep a constant temperature, which was set at 25 ºC in this work. The jar was covered with a PTFE plate on top with four exposure holes through which the WMSs were inserted. The PTFE plate was provided with a plastic holder for easy removal and sealed against the jar walls with a Viton O-ring wrapped with Teflon® tape. Another piece of ¼" stainless steel tubing was inserted through the PTFE plate to pass the overflow solution to a stainless steel union tee which was connected from one end to a rubber tube to dispose of the

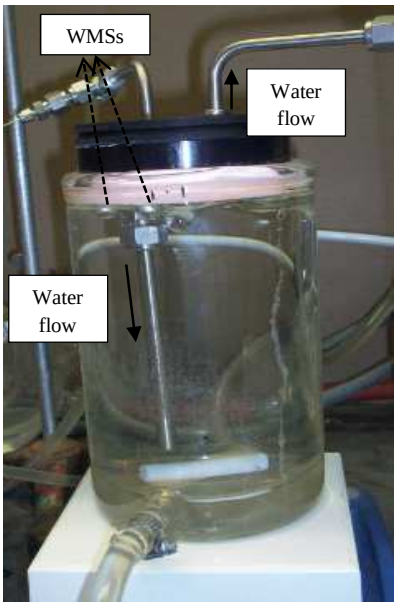

Figure 3-2: Exposure cell used to expose the WMS to water

solution as a chemical waste. The third end of the union tee was plugged with a septum through which an SPME device was inserted to measure the concentrations. In this system, the concentrations inside the exposure jar were controlled by controlling the concentrations in the spiking solution, its flow rate, and the water flow rate. The system was left to equilibrate for several hours before starting any exposure.

3.1.4. Determination of the analyte concentrations using the SPME device

The SPME fiber used had a 100 µm PDMS coating and a fused silica core (available from Sigma-Aldrich, Canada). The SPME device was directly immersed into the overflow solution for 45 min to reach equilibrium. SPME calibration was performed by preparing external standards in 40 ml glass vials with open top cap and Teflon/Silicon septum (purchased from Chromatographic Specialties Inc.). The vials were filled with distilled water sealed with no headspace and with magnetic stir bars enclosed. The volume of the water inside the vial was determined based on its weight considering that the water density is 1 g/cm^3. The water in each vial was then spiked with 21 µl of the analyte solution in methanol using a 100 µl glass syringe.

The concentrations in the spiking solution differed according to the desired concentrations in the aqueous solution. When the solution was uniform after few seconds of stirring, the needle of the syringe was removed and replaced by the SPME needle. The SPME fiber was exposed for 45 min to reach equilibrium before it was removed and analyzed in the GC-MS using the same SIM-mode method described in Section (3.1.2) with 2 min desorption time at 250 °C, splitless injection.

3.2. Results and discussion

3.2.1. Theoretical assessment

As previously explained, the amount of analytes collected by the sampler when sampling from air can be calculated by eq. (1.2) based on Fick's first law. Similarly, when sampling from water, the mass of the analyte M (kg) collected during the time of exposure t (min) is calculated by eq. (3.1):

$$\frac{M}{t} = D\frac{A}{L_m}(C_{mw} - C_{ms}) \qquad (3.1)$$

in which C_{mw} is the analyte concentration at the water-membrane interface (kg/cm^3). Assuming that the sorbent acts as a zero sink, C_{ms} is approximately zero. Also, similar to eq. (1.3), the concentration at the water-membrane interface at a given temperature is given by eq. (3.2):

$$C_{mw} = K_{wm} C_0 \qquad (3.2)$$

In this equation, K_{wm} is the partition coefficient of the analyte between water and the PDMS membrane, and C_0 is the concentration of the analyte in the water. Considering that D and K_{wm}

are constants at a given temperature, the calibration constant of the sampler toward the analyte when sampling from water (k_w) can be defined as follows:

$$k_w = L_m/(DK_{wm}A) \qquad (3.3)$$

Accordingly, eq. (3.1) can be written as in eq. (3.4)

$$C_0 = k_w \frac{M}{t} \qquad (3.4)$$

K_{wm}, the analyte partition coefficient between water and the membrane, is correlated to the analyte partition coefficient between air and the membrane (K_{am}) by eq.(3.5) [64, 65].

$$K_{wm} = K_{am}\, K_{aw} \qquad (3.5)$$

In this equation, K_{aw} is Henry's law coefficient for the analyte of interest.

By considering eq. (3.5), eq. (3.3) can be written as follows:

$$k_w = \frac{L_m}{DK_{am}K_{aw}A} \qquad (3.6)$$

By comparing equations (1.4) and (3.6), one concludes that

$$k_w = \frac{k_a}{K_{aw}} \qquad (3.7)$$

meaning that the calibration constant for an analyte when sampling from water (k_w) can be estimated from its calibration constant value in air sampling (k_a) and its Henry's constant. The calibration constants of the WMS towards the studied analytes were measured experimentally

and compared to the values obtained from eq. (3.7). Table 3-2 demonstrates the calculated values of k_w towards the compounds studied in this part of the work based on the above described hypothesis.

Table 3-2: Theoretical calibration constant values of the WMS towards the studied compounds in water and the properties of these compounds

Compound	**Solubility in water (mole/L)**	**M (g/mole)**	**C_{sat} (g/L)**	**K_{aw}** [65]	**k_a (calibration constant in air) (min/ml)** [14]	**k_w (calibration constant in water) (min/ml)**
Benzene	0.022	78.1	1.748	0.224	0.41	1.85
Toluene	0.006	92.2	0.553	0.251	0.21	0.85
chloroform	0.071	119.4	8.454	0.145	0.51	3.56
TCE	0.008	131.4	1.091	0.490	0.31	0.62
O-Xylene	0.002	106.2	0.191	0.204	0.11	0.55
1,1-DCE	0.026	96.9	2.519	1.259	1.22	0.97
Ethylbenzene	0.002	106.2	0.170	0.316	0.14	0.43

3.2.2. Preliminary results

Several experiments were performed for different exposure times using the experimental setup described above. In each experiment, 3 to 4 samplers were simultaneously exposed for a predetermined period of time. The samplers were desorbed after sampling using the method explained in Section (2.1.4) to be subsequently analyzed by GC-MS. The calibration constant (k_w) value for each compound was calculated from eq. (3.1) after determining the mass of the analyte trapped by the sorbent and the concentration in the exposure jar (determined by SPME measurement as explained in Section (3.1.4)) .

The results of these experiments are presented in Table 3-3. By examining the RSD values, poor reproducibility can be seen between samplers in most of the experiments. Additionally, considerable variation between the calibration constants obtained from different experiments was found. The experimental values of the calibration constants presented in this Table were also incomparable with the theoretical values shown in Table 3-2.

Table 3-3: Calibration constant values obtained from different preliminary experiments

Compound	Concentration (µg/ml)	Exposure time (min)	k (ave) (min/ml)	n	STD	RSD (%)
1,1-DCE	4.65E-02	1427	21.16	3	0.931	4.4
	4.65E-02	2964	27.77	3	3.387	12.2
	3.28E-04	1456	7.33	4	2.323	31.7
	2.61E-04	2880	4.43	4	1.385	31.3
	3.55E-04	5715	8.08	4	3.565	44.2
Chloroform	1.42E-02	1452	14.10	3	1.769	12.5
	3.60E-02	1427	16.75	3	0.330	2.0
	3.60E-02	2964	19.65	3	1.284	6.5
	5.14E-04	1456	12.75	4	1.515	11.9
	1.45E-02	2880	8.92	4	1.970	22.1
	7.92E-03	5715	19.15	4	6.706	35.0
Benzene	4.13E-03	1452	9.97	3	1.868	18.7
	1.88E-02	1427	10.28	3	0.345	3.4
	1.88E-02	2964	12.62	3	1.078	8.5
	4.58E-04	1456	7.35	4	1.831	24.9
	4.27E-04	2880	7.23	4	1.666	23.1
	2.99E-04	5715	7.60	4	2.746	36.1
Trichloroethylen	2.89E-03	1452	4.24	3	1.075	25.3
	1.57E-02	1427	4.81	3	0.942	19.6
	1.57E-02	2964	7.19	3	0.839	11.7
	3.19E-04	1456	4.96	4	1.932	39.0
	2.14E-04	2880	2.69	4	1.123	41.7
	2.63E-04	5715	4.59	4	2.191	47.8
Toluene	2.57E-03	1452	4.05	3	1.024	25.3
	1.92E-02	1427	6.03	3	0.334	5.5
	1.92E-02	2964	7.29	3	1.064	14.6
	3.63E-04	1456	6.72	4	2.984	44.4
	4.65E-04	2880	6.90	4	2.605	37.8
	2.49E-04	5715	5.46	4	2.989	54.7
Ethylbenzene	2.20E-03	1452	2.89	3	0.909	31.5
	1.64E-02	1427	3.77	3	0.293	7.8
	1.64E-02	2964	4.36	3	0.836	19.2
	3.79E-04	1456	5.86	4	2.788	47.6
	1.92E-04	2880	2.36	4	1.087	46.1
	2.37E-04	5715	4.26	4	2.598	61.0
o-Xylene	3.88E-03	1452	6.73	3	1.885	28.0
	1.55E-02	1427	4.74	3	0.319	6.7
	1.55E-02	2964	5.47	3	0.962	17.6
	3.11E-04	1456	5.84	4	2.692	46.1
	2.61E-04	2880	4.06	4	1.671	41.2
	2.14E-04	5715	4.74	4	2.773	58.5

The likely explanation of these observations is permeation of water through the membrane onto the adsorbing phase, leading to blocking of the active sites on the sorbent. This, in turn, means that the concentration at the sorbent-membrane interface was not zero as assumed

in the theory. Another factor that may have an effect on the sampling process was air bubble formation at the surface of the membrane during the exposure period.

3.2.3. Effect of sorbent type modification

In this part, the effect of changing the type of the sorbent on the performance of the WMS in water sampling was examined. For this purpose, four samplers were simultaneously exposed: two prepared as previously described with Anasorb 747 as the sorbent, while the other two samplers were prepared with another sorbent named Dowex® Optipore® V493 (Purchased in a 100 g quantity from Sigma-Aldrich, Canada). This sorbent, as described by the manufacturer (DOW product information), is a highly cross-linked styrenic polymer of high capacity (1188 m^2/g surface area vs. 980 m^2/g surface area of Anasorb 747). Dowex® Optipore® V493 is also described by the manufacturer to have higher hydrophobicity than activated carbon and to be suitable for vapor applications. Therefore, this sorbent was selected to study the impact of changing the sorbent type on the WMS performance in sampling from water. Taking into consideration the difference in capacity between the two sorbents, 202 mg of Dowex® Optipore® V493 was used in each sampler with this sorbent, whereas the two samplers with Anasorb 747 were prepared with 250 mg of the sorbent as previously explained. Both sorbents were similarly desorbed and analyzed as described earlier in this chapter. The comparison was based on five out of the seven analytes studied in this work due to blank peaks interference with toluene and ethylbenzene after desorbing Dowex® Optipore® V493 using CS_2. Student's t-test (paired two sample for means) was used to determine the significance of the sorbent type on sampling efficiency. Table 3-4 presents the masses collected by the samplers in three experiments and the resulting t_{Stat} and $t_{Critical}$ for each compound. The results demonstrate no significant effect of changing the sorbent type on the measured values of the calibration constants for all compounds

(t_{Stat} smaller than $t_{Critical}$ for all the studied compounds). Figure 3-3 shows two chromatograms obtained from two samplers exposed simultaneously with different types of sorbents. The similarity between the two chromatograms can be seen in this figure, which supports the previous conclusion.

Table 3-4: Results of two-tailed, paired, student t-test used to examine the effect of sorbent type modification on the uptake rates of the WMS in water sampling

Compound	Experiment	Concentration (µg/ml)	time (min)	Sorbent type	k (ave) (min/ml)	n	RSD (%)	t-Test: Paired Two Sample for Means	
								t Stat	t Critical 2-tail
1,1-DCE	1	2.10E-03	1422	Anasorb 747	15.51	2	23.4	0.013	4.303
				Dowex Optipore	14.25	2	8.5		
	2	2.34E-02	308	Anasorb 747	10.77	2	8.1		
				Dowex Optipore	12.08	2	7.6		
	3	2.48E-02	1138	Anasorb 747	7.71	2	3.9		
				Dowex Optipore	7.69	2	23.7		
Chloroform	1	1.14E-02	1422	Anasorb 747	14.56	2	56.0	0.533	4.303
				Dowex Optipore	12.59	2	6.5		
	2	4.55E-02	308	Anasorb 747	15.20	2	3.2		
				Dowex Optipore	18.18	2	7.5		
	3	4.78E-02	1138	Anasorb 747	12.74	2	2.6		
				Dowex Optipore	14.06	2	11.9		
Benzene	1	5.56E-04	1422	Anasorb 747	8.98	2	52.6	-0.426	4.303
				Dowex Optipore	7.00	2	11.2		
	2	2.74E-02	308	Anasorb 747	14.63	2	4.6		
				Dowex Optipore	15.76	2	7.3		
	3	2.72E-02	1138	Anasorb 747	11.25	2	2.1		
				Dowex Optipore	10.95	2	21.4		
TCE	1	8.68E-04	1422	Anasorb 747	9.95	2	60.5	-0.056	4.303
				Dowex Optipore	6.86	2	25.0		
	2	5.58E-02	308	Anasorb 747	19.20	2	6.4		
				Dowex Optipore	22.39	2	10.6		
	3	5.39E-02	1138	Anasorb 747	11.16	2	2.6		
				Dowex Optipore	10.76	2	33.0		
o-Xylene	1	8.85E-04	1422	Anasorb 747	0.86	2	37.2	-2.072	4.303
				Dowex Optipore	0.62	2	19.1		
	2	1.82E-02	308	Anasorb 747	9.31	2	4.5		
				Dowex Optipore	8.36	2	6.7		
	3	1.89E-02	1138	Anasorb 747	8.64	2	0.3		
				Dowex Optipore	6.63	2	36.9		

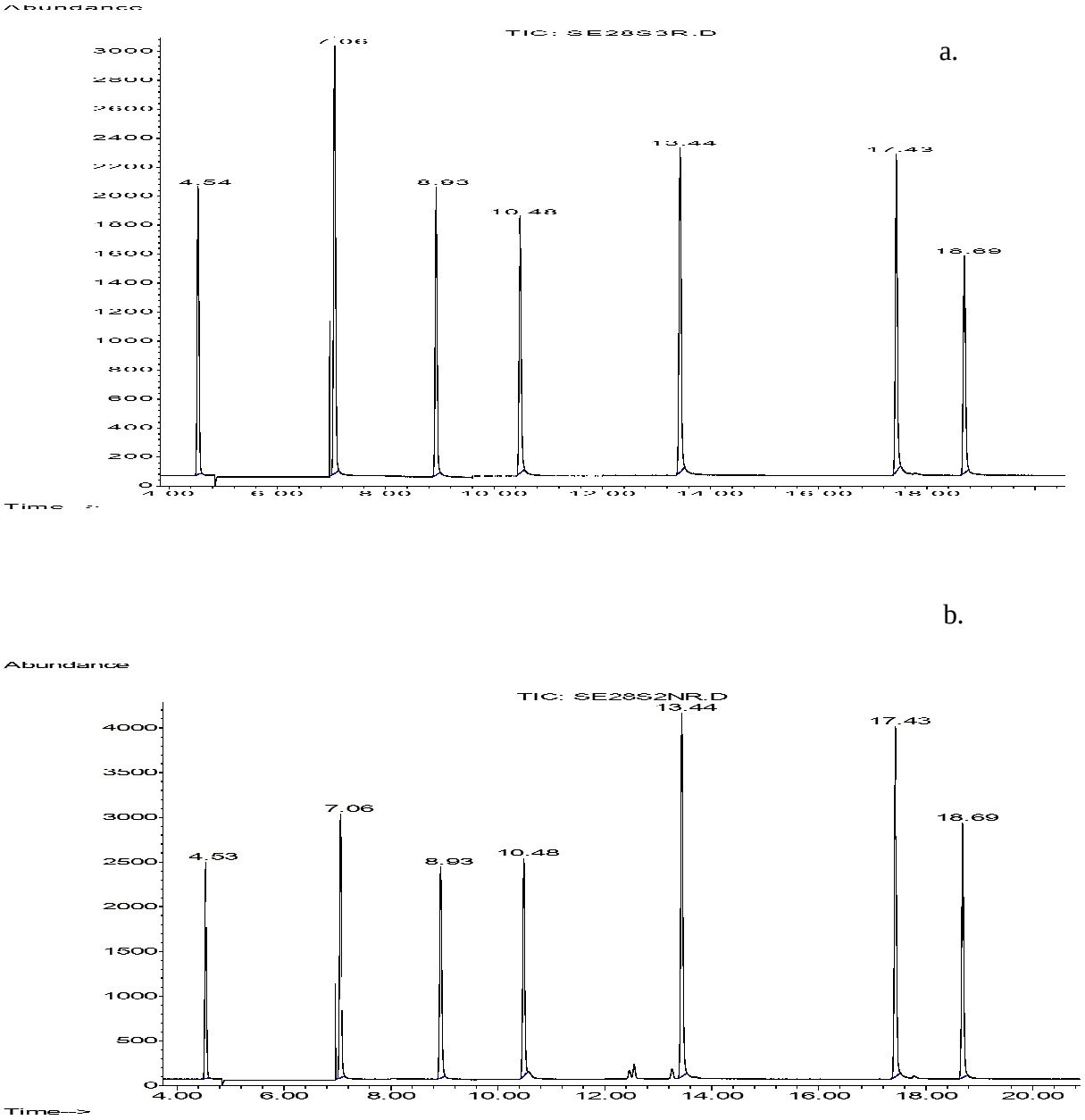

Figure 3-3: Chromatograms obtained from the analysis of two samples collected by means of two WMSs exposed under the same conditions using different types of sorbents: a. Anasorb 747b, b. Dowex® Optipore® V493

3.2.4. Extraction profiles

In this section, several experiments were completed using the WMS prepared with Anasorb 747. First, four exposures were performed at different exposure times and constant concentrations (~ 4 ppb) for all analytes. Four samplers were simultaneously exposed in each experiment. The average peak area in the chromatograms after the analysis was plotted versus the time of exposure as shown in Figures 3-4 and 3-5. The calibration constants obtained from these experiments are shown in Table 3-5. The plots presented in Figures 3-4 and 3-5 demonstrate proportionality between the collected masses of all analytes and the exposure time, which implies that the sampler can be successfully employed in sampling from water (although the calibration constant values obtained from these experiments still did not comply with the theory). Nevertheless, significant variation between replicates could be seen in the plots. This variation can also be seen in Table 3-5 between samplers in each experiment, considering the high RSD values.

In another set of experiments, the mass collected by the WMS, represented by the peak area, was studied as a function of the concentration level. Four exposures, with four replicates in each experiment, were completed for one day each and at different concentrations. Table 3-6 shows the results of these experiments with the corresponding k_w values. Figures 3-6 and 3-7 present the average peak area, obtained after the analysis, plotted against the concentration levels of six analytes. Proportionality between the collected mass of an analyte and the concentration of that analyte is observed in these figures; however, lack of reproducibility is demonstrated by the error bars in the figures and the high RSD values in Table 3-6.

Table 3-5: Results of the analysis of WMSs exposed for different exposure times and the corresponding calibration constant values

Compound	Exposure time (min)	Average peak area	STD	RSD (%)	M (µg)	k_w (min/ml)
1,1-DCE	360	15779	3805	24.1	0.259	5.03
	1440	63622	34745	54.6	0.662	7.88
	2837	131582	32849	25.0	1.233	8.33
	4373	147330	58266	39.5	1.366	11.60
Benzene	360	35751	12529	35.0	0.118	11.01
	1440	132469	53215	40.2	0.647	8.07
	2837	230796	49713	21.5	1.184	8.68
	4373	301457	106408	35.3	1.570	10.09
TCE	360	23155	7882	34.0	0.368	3.54
	1440	124787	66210	53.1	1.466	3.56
	2837	245955	73941	30.1	2.776	3.70
	4373	321818	142382	44.2	3.595	4.41
Toluene	360	32898	11379	34.6	0.091	14.35
	1440	178931	101674	56.8	0.802	6.50
	2837	345707	109015	31.5	1.615	6.37
	4373	509435	223580	43.9	2.413	6.57
Ethylbenzene	360	40175	14692	36.6	0.413	3.16
	1440	289095	196423	67.9	1.277	4.09
	2837	609625	233038	38.2	2.388	4.30
	4373	958522	448950	46.8	3.598	4.40
o-Xylene	360	28287	10176	36.0	0.398	3.28
	1440	192991	127029	65.8	1.025	5.09
	2837	408186	154639	37.9	1.845	5.57
	4373	651851	311171	47.7	2.773	5.71

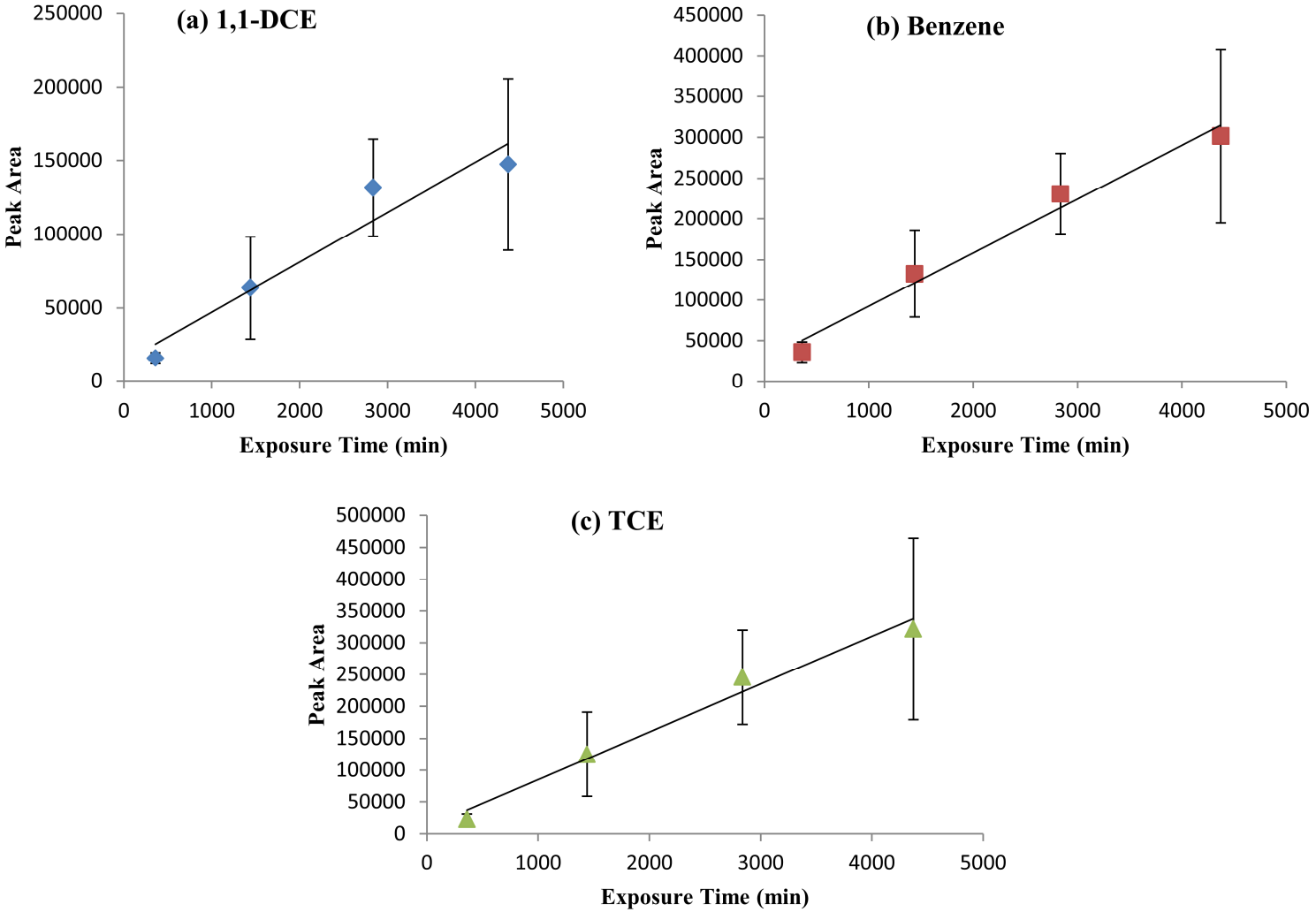

Figure 3-4: Extraction time profiles of (a) 1,1-DCE, (b) benzene, and (c) TCE

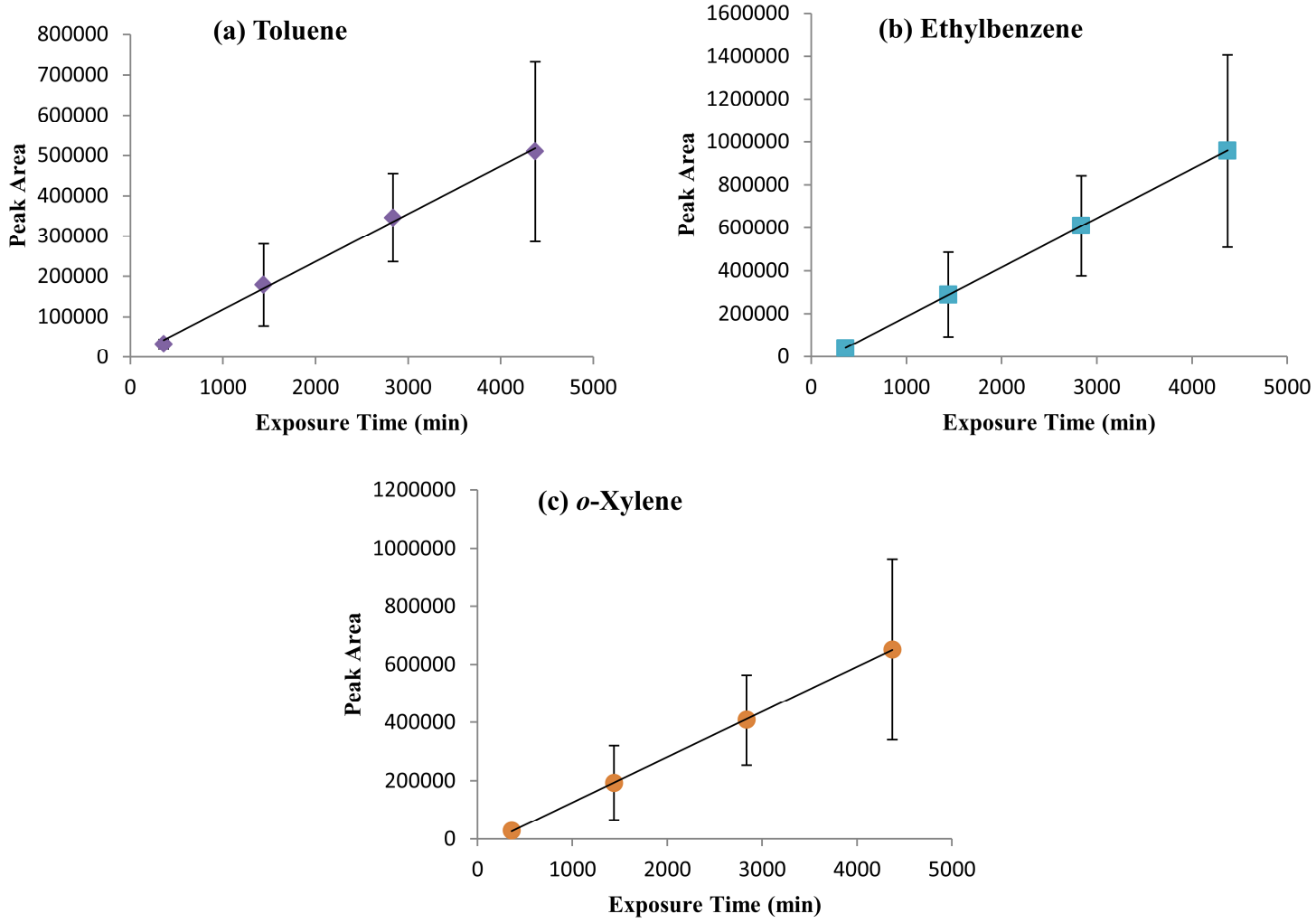

Figure 3-5: Extraction profiles with time for (a) toluene, (b) ethylbenzene, and (c) *o*-xylene

Table 3-6: Results of sampling VOCs from water for one day at different concentrations

Compound	Concentration (µg/ml)	Average peak area	STD	RSD (%)	M (µg)	k_w (min/ml)
1,1-DCE	3.62E-02	509130	311088	61.1	4.409	11.83
	1.81E-02	290314	62753	21.6	2.569	10.16
	3.62E-03	32535	16908	52.0	0.400	13.03
	1.81E-03	24105	11605	48.1	0.329	7.92
Benzene	3.62E-02	589170	333006	56.5	3.142	16.60
	1.81E-02	363858	76720	21.1	1.911	13.65
	3.62E-03	40667	20685	50.9	0.145	35.90
	1.81E-03	25276	12187	48.2	0.061	42.60
TCE	3.62E-02	638003	406738	63.8	7.012	7.44
	1.81E-02	368045	108669	29.5	4.095	6.37
	3.62E-03	36609	19424	53.1	0.513	10.16
	1.81E-03	26025	12621	48.5	0.399	6.54
Toluene	3.62E-02	894694	572631	64.0	4.289	12.16
	1.81E-02	507205	160643	31.7	2.402	10.86
	3.62E-03	41228	20756	50.3	0.132	39.67
	1.81E-03	25647	12606	49.2	0.056	46.92
Ethylbenzene	3.62E-02	1414280	988335	69.9	5.178	10.08
	1.81E-02	814561	313332	38.5	3.099	8.42
	3.62E-03	53211	27323	51.3	0.459	11.38
	1.81E-03	36003	20024	55.6	0.399	6.54
o-Xylene	3.62E-02	963584	665730	69.1	3.961	13.17
	1.81E-02	553474	210074	38.0	2.398	10.88
	3.62E-03	36356	18045	49.6	0.429	12.17
	1.81E-03	22710	11947	52.6	0.377	6.92

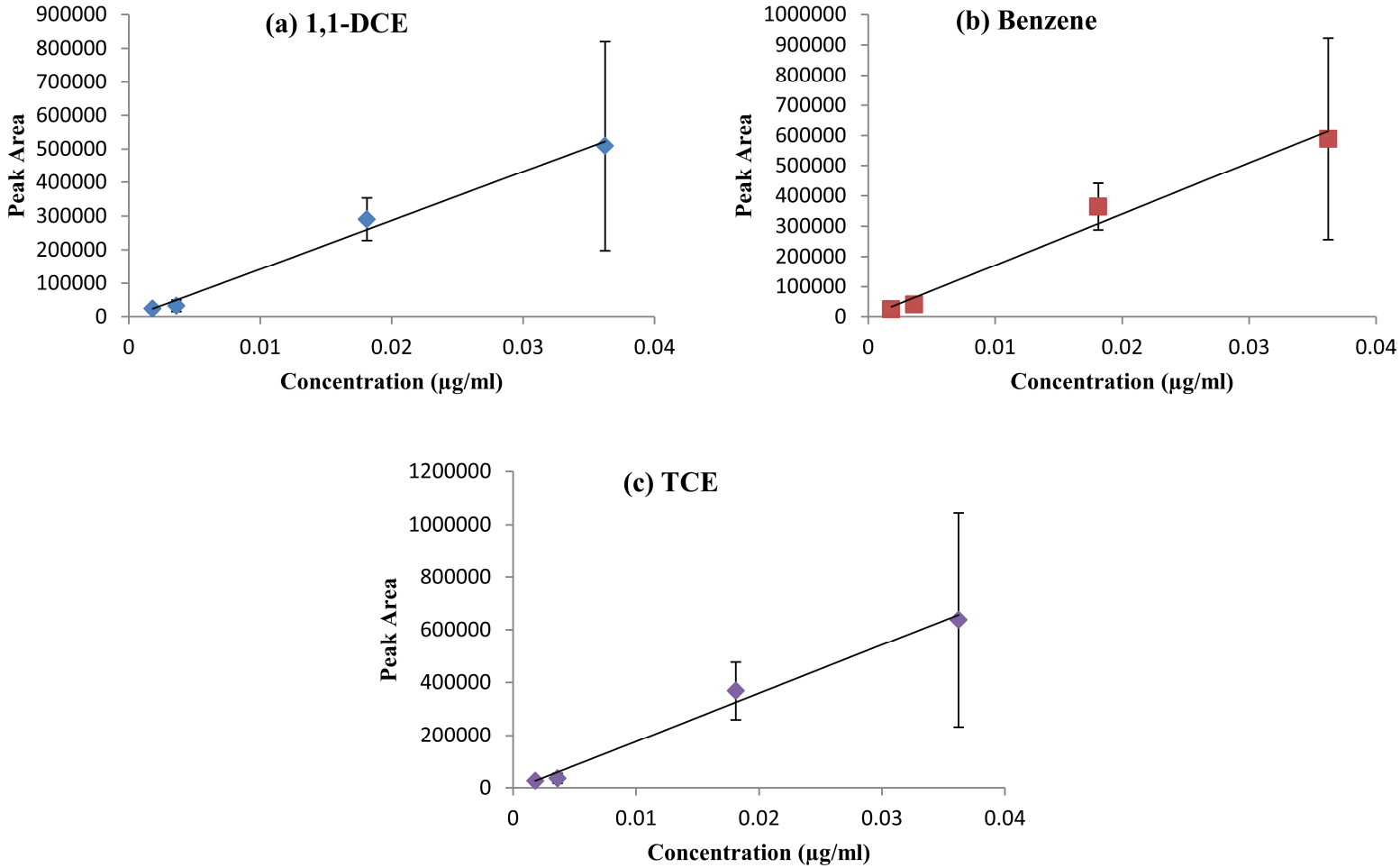

Figure 3-6: Mass extracted by the WMS as a function of concentration for (a) 1,1-DCE, (b) benzene, and (c) TCE

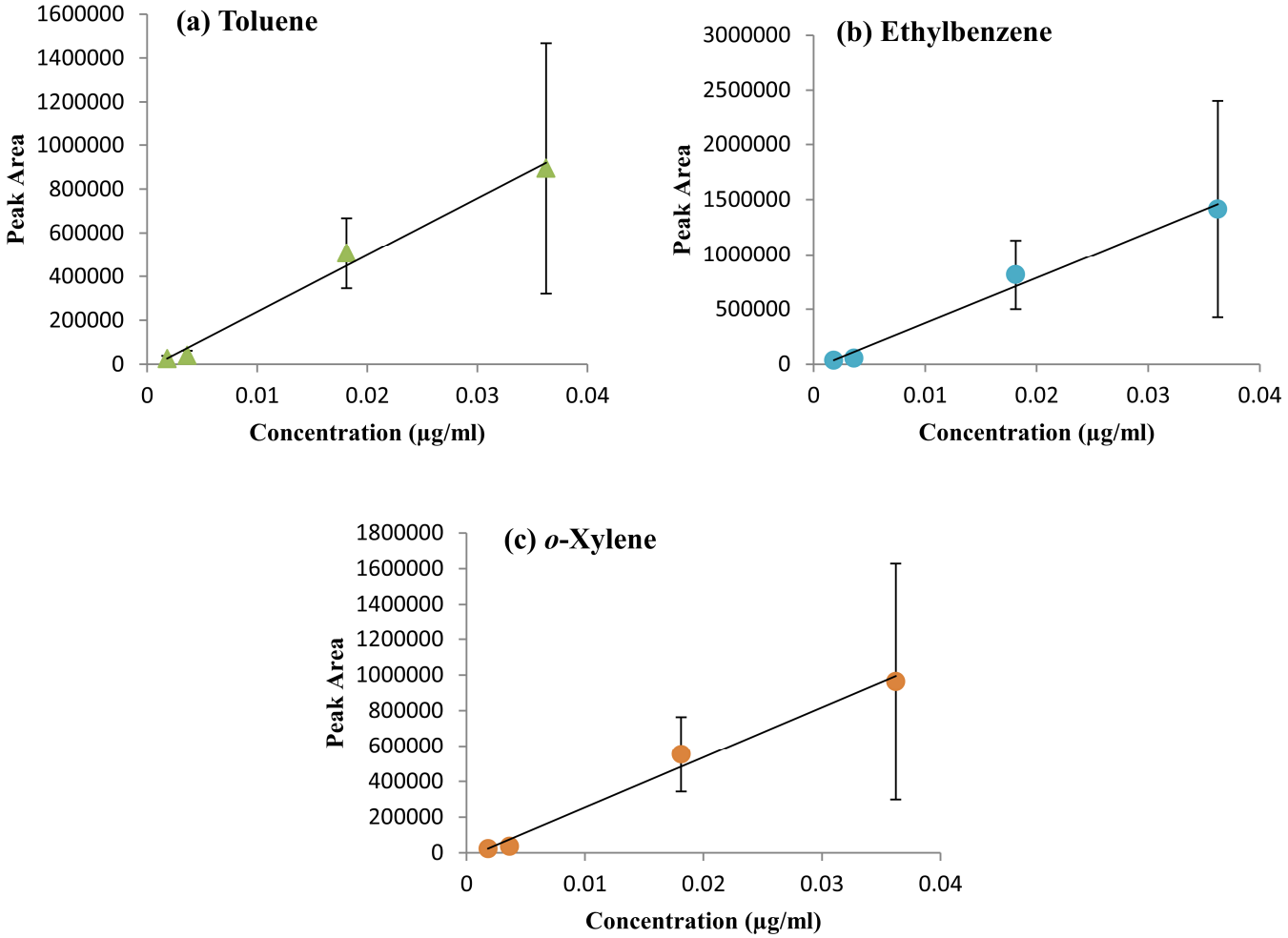

Figure 3-7: Mass extracted by the WMS as a function of concentration for (a) toluene, (b) ethylbenzene, and (c) o-xylene

The poor reproducibility between samplers can be attributed to bubble formation at the surface of the membrane as shown in Figure 3-7. These bubbles at the surfaces of different samplers were not identical, but differed in shape and size. The mechanism of mass transfer within the bubbles (diffusion) has an impact on the total kinetics of the mass transfer into the sampler; therefore, the uptake rate value towards an analyte and the reproducibility are affected by these bubbles. In the case of these experiments, the problem of bubble formation was caused by high levels of dissolved gases in the pressurized tap water, unlike the case of sampling from groundwater, which has significantly lower levels of dissolved gases.

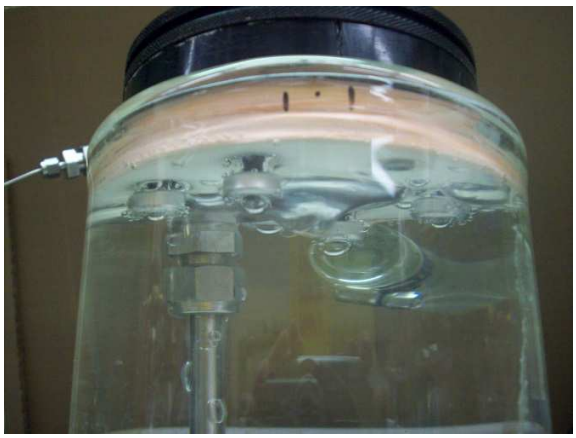

Figure 3-8: Bubble formation at the surface of the membrane

In order to overcome this problem in this work and to study the performance of the WMS in absence of these bubbles, a modification was made to the experimental setup presented in Section (3.1.3) by adding a mechanical stirrer close to the surfaces of the samplers to remove the bubbles as shown in Figure 3-8. The stirrer consisted of a custom-made stainless steel blade attached to a shaft inserted though the top PTFE plate and surrounded by a PTFE sleeve at the insertion point to minimize the friction effects. The shaft was connected to a motor (taken from GSW DIAMOND pump) held by a holder attached to an aluminum stand with an adjustable

plate that can be vertically slid to adjust the stirrer height. The stand was connected to an aluminum base on which the exposure cell was placed. The motor's circulation speed was controlled by means of a Powerstat® variable autotransformer (Type 3PN116B, Superior Electric Company, CT).

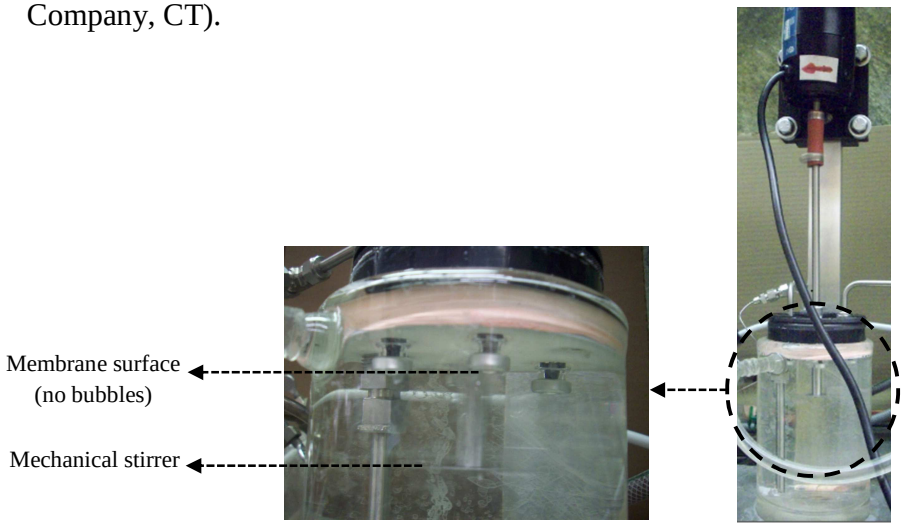

Figure 3-9: Samplers exposed to water after inserting the mechanical stirrer for bubble removal

The extraction profiles were studied after the modification at two concentration levels: the first set of experiments was performed at approximately 4 ppb concentration level for all compounds, whereas the second set was completed at approximately 10 ppb level. The concentration of chloroform was slightly higher than the other compounds due to its presence in tap water. The concentration of this compound was not accurately quantified but was checked for stability during the exposures. In these experiments, the analysis was done using splitless injection in the GC to increase the sensitivity of the method.

The results of these experiments are presented in Table 3-7 (at ~4 ppb concentration level) and Table 3-8 (at ~10 ppb concentration level). These tables show reasonable reproducibility between replicates in each experiment, considering the values of RSD which are lower than the values achieved in the previous experiments before the modification. Higher

reproducibility between the calibration constant (k_w) values, obtained at different exposure times and at both concentration levels, can also be seen, taking in consideration that the measurement of the calibration constant is very sensitive to any experimental error or variation between experiments. The mass collected by the sampler was plotted against the exposure time at both concentration levels for the studied compounds as presented in Figure 3-9. This figure illustrates proportionality between the collected mass and the time of exposure for all compounds at both levels of concentration, meaning that the WMS showed successful implementation in sampling from water. Nonetheless, when compared to the theoretical values presented in Table (3-2), the experimental calibration constant values presented in Tables 3-7 and 3-8 were found to be significantly different, which means that the sampling process was affected by factors that were not considered in the theory.

Table 3-7: Results of sampling from water for different exposure times at ~4 ppb concentration level after the setup modification

Compound	Exposure time (min)	Average collected mass (µg)	STD	RSD (%)	k_w (min/ml)
1,1-DCE	180	0.033	0.003	8.8	19.72
	435	0.113	0.011	9.4	13.99
	727	0.205	0.012	5.7	12.85
	1204	0.242	0.018	7.3	17.97
Benzene	180	0.062	0.003	4.0	10.20
	435	0.136	0.014	10.6	11.34
	727	0.220	0.011	5.2	11.61
	1204	0.288	0.010	3.5	14.67
TCE	180	0.047	0.007	16.1	14.09
	435	0.136	0.030	22.2	11.86
	727	0.249	0.021	8.3	10.50
	1204	0.306	0.013	4.4	14.06
Toluene	180	0.046	0.006	13.4	14.66
	435	0.127	0.019	14.9	12.83
	727	0.223	0.017	7.6	12.06
	1204	0.292	0.017	5.9	15.26
Ethylbenzene	180	0.051	0.009	17.0	13.14
	435	0.143	0.035	24.6	11.40
	727	0.252	0.027	10.9	10.48
	1204	0.313	0.018	5.9	13.89
o-Xylene	180	0.049	0.007	13.9	12.60
	435	0.137	0.028	20.2	11.09
	727	0.244	0.023	9.5	10.16
	1204	0.308	0.015	4.7	13.23

Table 3-8: Results of sampling from water for different exposure times at ~10 ppb concentration level after the setup modification

Compound	Exposure time (min)	Average collected mass (µg)	STD	RSD (%)	k_w (min/ml)
1,1-DCE	182	0.111	0.018	16.7	24.27
	272	0.271	0.028	10.4	14.57
	460	0.323	0.067	20.9	21.21
	737	0.583	0.065	11.1	18.41
	1362	1.102	0.186	16.9	18.22
Benzene	182	0.142	0.006	4.5	18.05
	272	0.201	0.007	3.4	19.03
	460	0.313	0.010	3.3	20.61
	737	0.516	0.033	6.4	20.10
	1362	1.042	0.115	11.0	18.50
TCE	182	0.163	0.009	5.4	15.97
	272	0.247	0.018	7.4	15.78
	460	0.393	0.023	5.9	16.78
	737	0.663	0.048	7.2	15.94
	1362	1.336	0.143	10.7	14.70
Toluene	182	0.183	0.011	6.2	14.68
	272	0.274	0.015	5.4	14.66
	460	0.463	0.024	5.1	14.70
	737	0.762	0.060	7.9	14.34
	1362	1.592	0.181	11.4	12.75
Ethylbenzene	182	0.164	0.009	5.5	16.02
	272	0.256	0.023	9.0	15.38
	460	0.484	0.033	6.8	13.72
	737	0.708	0.063	8.9	15.08
	1362	1.511	0.171	11.4	13.11
o-Xylene	182	0.128	0.007	5.5	19.25
	272	0.196	0.015	7.7	18.87
	460	0.369	0.021	5.6	16.91
	737	0.552	0.048	8.7	18.19
	1362	1.182	0.137	11.6	15.76

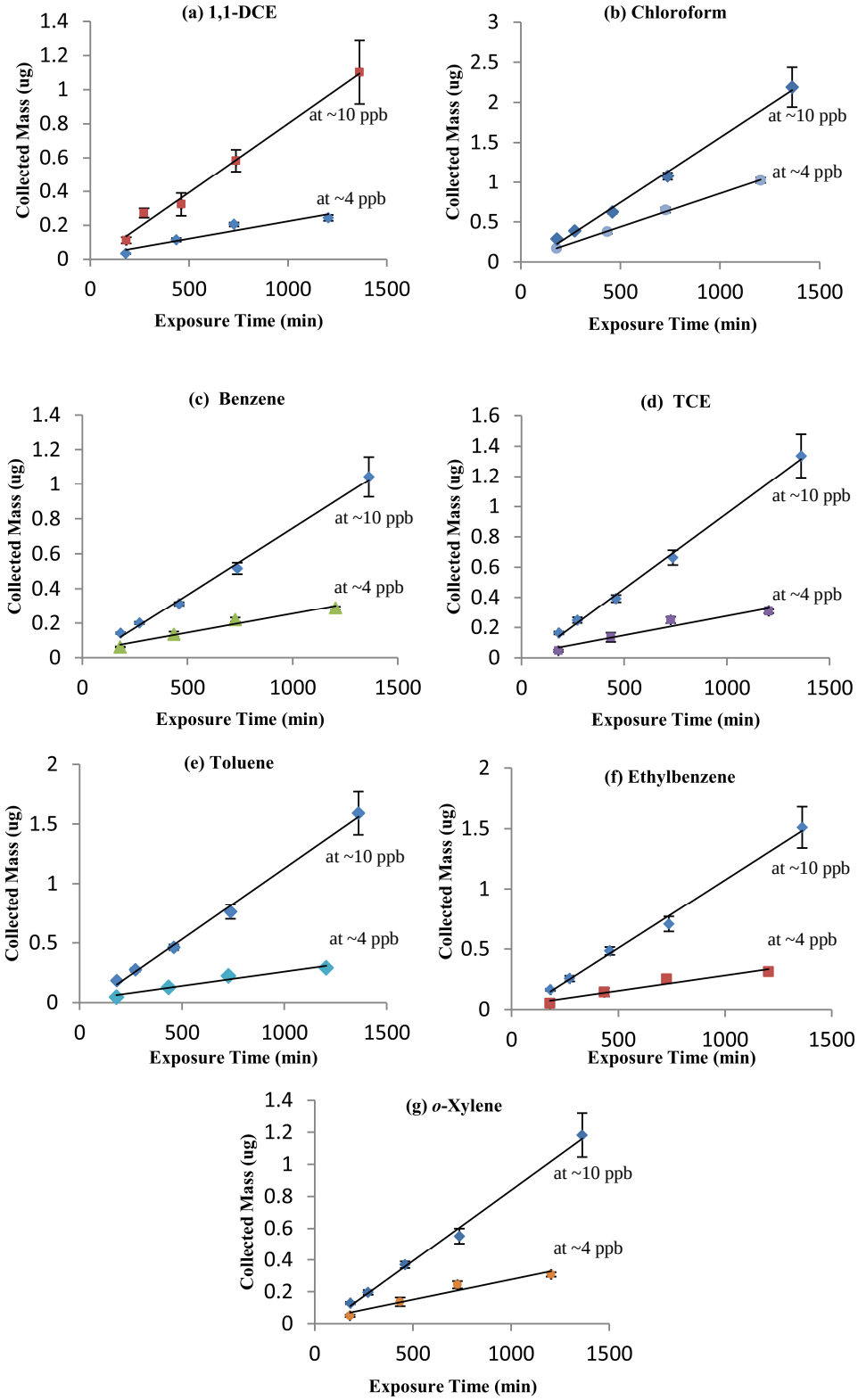

Figure 3-10: Extraction Profiles of (a) 1,1-DCE, (b) chloroform, (c) benzene, (d) TCE, (e) toluene, (f) ethylbenzene, and (g) *o*-xylene from water at two concentration levels using the WMS

3.2.5. Detection and quantification limits

The limit of detection (LOD) and the limit of quantification (LOQ) were estimated based on the signal to noise ratio (S/N) obtained from analyzing samples collected in three-hour exposure at ~ 0.0036 µg/ml concentration. The LOD and LOQ values are presented in Table 3-9, in which low detection limits are seen (in the low to sub-ppb range) for all compounds. The LOD values for TCE, toluene, ethylbenzene, and *o*-xylene are in the tens of ppt range, which is very low after only 3 hours of exposure.

Table 3-9: Estimated LOD and LOQ values for the VOCs sampled from water using the WMS

Compound	LOD (µg/ml)[a]	LOQ (µg/ml)[b]
1,1-DCE	1.26E-03	4.21E-03
Benzene	3.28E-04	1.09E-03
TCE	5.91E-05	1.97E-04
Toluene	8.38E-05	2.79E-04
Ethylbenzene	1.59E-05	5.30E-05
o-Xylene	1.96E-05	6.55E-05

[a]S/N ≥ 3 and [b]S/N ≥ 10

3.2.6. Conclusions and recommendations

Seven VOCs, considered as important groundwater pollutants, were studied in this work. The WMS demonstrated linear uptake of the targeted compounds over the studied period of time and at different concentration levels. Very low detection limits were achieved for all studied compounds. Thus, the WMS can be considered a successful and simple tool for sampling VOCs from groundwater. The calibration constant values for the sampler towards the studied compounds were measured with a reasonable reproducibility. A theoretical relationship between the calibration constant of the WMS towards an analyte in air sampling and the calibration constant towards that analyte in water sampling was established; however, the experimental values of the calibration constants in water sampling did not comply with the theory. The discrepancy between the theoretical and the experimental values can be explained by water permeation through the membrane. Permeated water hinders the complete removal of the analytes at the membrane-sorbent interface. This means that the analyte concentrations at this interface are not zero unlike the theoretical assumption. Further experiments are recommended to minimize this effect by increasing the thickness of the membrane. Evaluating and optimizing the WMS performance in sampling from water using different types of sorbents are also recommended. Finally, examining the applicability of the sampler for long-term monitoring is an important step for future work.

4. CHAPTER FOUR: NEW METHOD FOR VOC EXTRACTION FROM BULK SOIL USING THE WMS

A new technique for extracting VOCs from bulk soil was introduced and examined in this chapter. The extraction was performed in this method by exposing the WMS to the headspace of the soil sample inside a sealed container. The principle of the method is that the WMS would remove any analyte partitioning into the soil headspace. Therefore, all sample content of VOCs would be collected by the sampler after sufficient time. The experiments presented in this chapter evaluated the possibility of achieving the desired exhaustive extraction and the effects of different parameters on the extraction efficiency.

4.1. Experimental

The WMS used in this part were prepared as described in Section (3.1.1). All chemicals were obtained as presented in Sections (2.1.2) and (3.1.2). The GC-MS system introduced in Section (2.1.5) was used. The GC-MS method employed in this part was similar to the one explained in Section (2.1.6) with the exception of the second ramp in the temperature program which was set at 30 °C/min up to 250 °C, held for 3 minutes. The compounds studied in this part and their ions used in the Selected Ion Monitoring (SIM) mode are presented in Table 4-1. The samples obtained from all experiments were desorbed before the analysis as described in Section (2.1.4).

Table 4-1: Ions used in the SIM mode analysis of samples obtained from bulk soil using the WMS

Compound	Ions used in the SIM mode (m/z)
Trichloroethylene (TCE)	95, 130, 132
Tetrachloroethylene (PCE)	166, 164, 131

4.2. Results and discussion

4.2.1. Initial experiments

The experimental method for extracting VOCs from bulk soil was initially designed, as shown in Figure 4-1, to expose the WMS to the headspace of the soil sample through a hole in the cap of the jar. Extracting from sandy soil was chosen to be a starting point to examine the feasibility of the method. Play sand (Fine Granulated washed sand, Alltreat Farms®) was used for this purpose. The sand was initially kept at ~130 °C for one day to dry it and to eliminate any possible contamination that might affect the results. 250 ml glass jars (bottle clear std w/m 8 oz, purchased from Fisher Scientific) were filled with 20 g of the sand and a hole was drilled in the center of each jar cap to insert the WMS, wrapped with Teflon® tape.

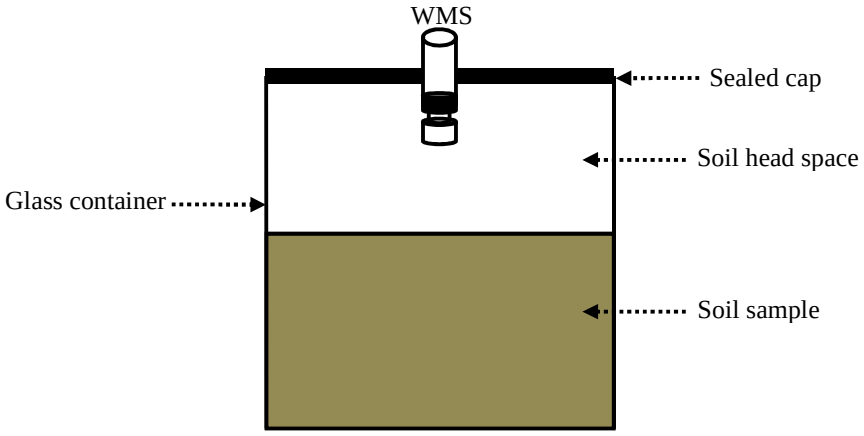

Figure 4-1: Initial setup for extracting VOCs from bulk soil using the WMS

In a preliminary experiment, three sand samples were prepared. Each of them was spiked with 5 µl of methanolic solution of TCE and PCE at the concentrations of 10.36 mg/ml and 12.28 mg/ml, respectively, using a 10 µl glass syringe. The cap of the container along with the WMS, inserted through the central hole, was then immediately put in place and tightened.

To minimize the loss of VOCs, the cap was tightened against Teflon® tape wrapped around the threads of the jar top and another piece of the tape was wrapped around the jar walls and the tightened cap. The samples were then left for seventeen days at room temperature before the samplers were retrieved and analyzed. The three samplers were able to extract 51%, 53%, and 55% of the spiked TCE and 59%, 60% and 61% of the PCE.

The effect of exposure time on the extraction efficiency, using the same experimental procedure presented above, was studied afterwards. In this experiment, twenty one samples of 20 g sand soil were spiked with 5 µl aliquots of a methanolic solution of 9.82 mg/mL of PCE and 10.16 mg/mL of TCE. The samplers were then exposed to the sand samples at room temperature for different times ranging from 1 to 21 days with 3 replicates for every time of exposure. The results are presented in Table 4-2 and Figure 4-2. The recovery of the two compounds did not show dependency on the time over the selected time range. The average amounts recovered were 60% of PCE and 59% of TCE. Similar recovery was achieved when three samplers were simultaneously exposed in the same jar. In this experiment, two sandy soil aliquots were prepared and spiked following the same method described above but with three samplers exposed in each jar through three holes in the cap. The purpose of this experiment was to verify that the lack of the extraction efficiency was not due to saturation of the sorbent. After one week exposure, the sums of the amounts recovered by the tree samplers in the first container were 52% of the expected amount of PCE and 49% of TCE, while the sums of the amounts recovered from the other container were 49% of PCE and 45% of TCE. These results suggested that the difference between the expected amount and the collected amount was due to loss of the analytes during preparation and spiking steps or during the exposure; otherwise, the concentration

gradient created by the sampler would have released the analytes adsorbed to the soil over the time.

Table 4-2: Average recoveries of TCE and PCE from sand at different exposure times

Exposure Time (min)	TCE Average Recovery (%)	STD	RSD %	PCE Average Recovery (%)	STD	RSD %
1480	54	4.8	8.9	61	3.7	6.1
4410	54	1.4	2.7	59	1.7	2.8
10170	62	3.0	4.8	61	3.1	5.0
14475	63	7.2	11.4	63	6.5	10.2
20205	56	7.5	13.3	55	6.9	12.6
24555	62	10.1	16.3	60	9.1	15.2
30315	64	1.2	1.8	61	1.9	3.1

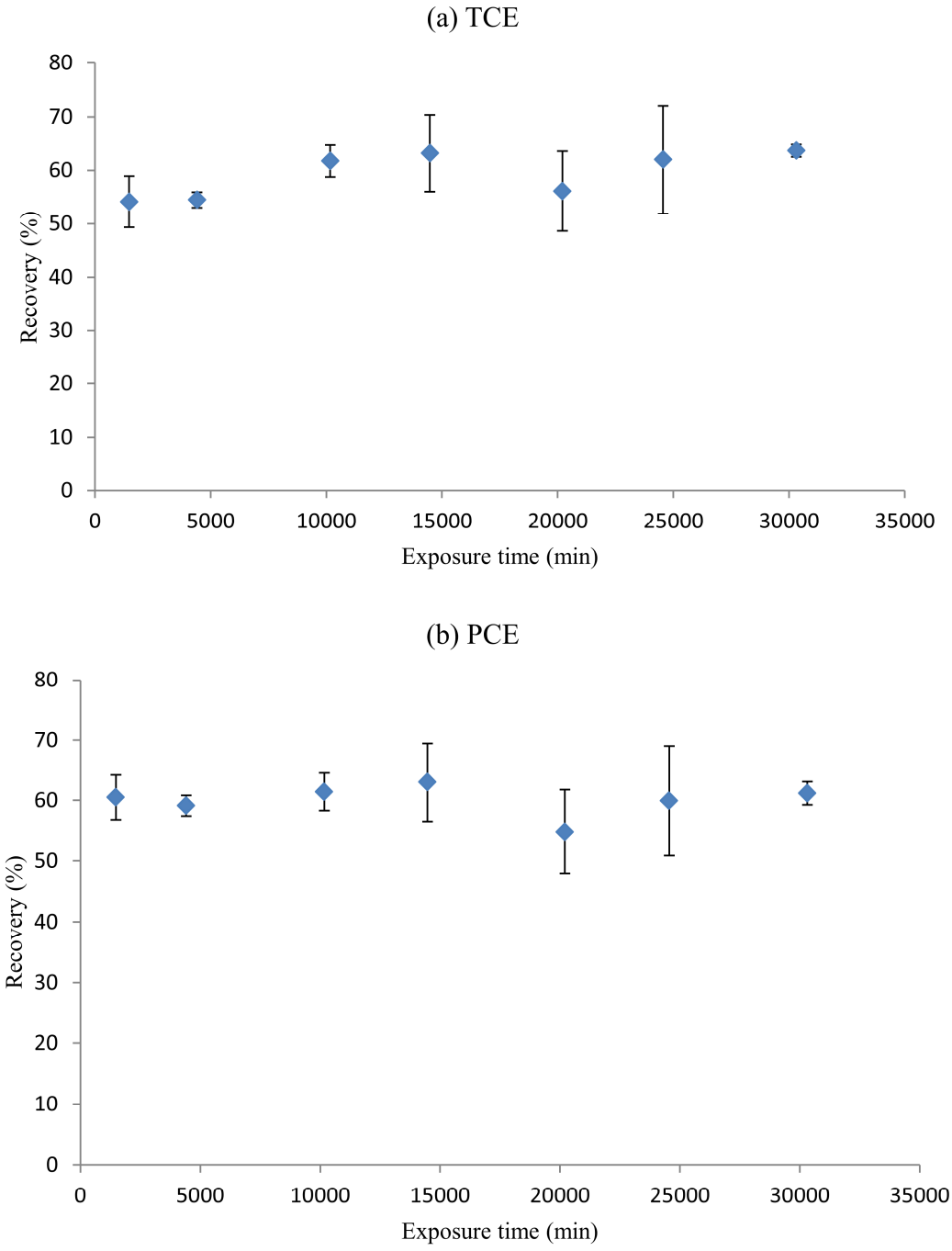

Figure 4-2: Recovery rate over time for (a) TCE and (b) PCE

4.2.2. Investigations for potential sources of analyte loss

Further studies were conducted to investigate the fate of the unrecovered amounts of the analytes. Several experiments were performed for this purpose. In all these experiments, an aqueous solution of the analytes was used for spiking.

4.2.2.1. Preparation of the spiking solution

The aqueous solutions were prepared in 40 ml glass vials with open top cap and Teflon/silicone septum (purchased from Chromatographic Specialties Inc.). The vials were filled with distilled water, sealed with no headspace and with magnetic stir bars enclosed. The volume of the water inside the vial was determined based on its weight. A solution in methanol was prepared with 50 mg/ml of TCE and similar concentration of PCE. A 30 µl aliquot of this solution was taken using a 100 µl glass syringe. The needle of the syringe was then wiped and inserted through the vial septum to inject the solution into the water. The needle was kept for a few seconds while the solution was stirred. The needle was subsequently removed to be replaces by the needle of a 500 µl gas-tight glass syringe. A 100 µl aliquot of the aqueous solution was taken to be spiked into the soil sample after wiping the needle. A fresh solution in a new vial was prepared for each individual sample to avoid loss of analytes from one sample to another through the pierced septum.

4.2.2.2. Assessment of potential leak of the analytes from the sample container

In the first experiment, three samples of 20 g of sand were prepared inside three containers similar to the containers used in the previous experiments but of smaller sizes (4 oz). The samples were spiked as described in Section (4.2.2.1) and sealed with the cap holding the WMS through the central hole as explained earlier. Each jar was placed inside another glass jar (16 oz), which was sealed with the cap and another sampler held in a central hole as well, as

shown in Figure 4-3, (a). After one week of exposure, the samplers were retrieved and analyzed. The results of these experiments, as presented in Table 4-3, demonstrate considerable amounts of the two compounds detected in the outer samplers, which means that these analytes escaped from the inner container (with the soil sample) to the outer container.

Table 4-3: Results of successive sampling of analytes using inner and outer samplers inserted through holes in the container caps

Sample	Recovery of TCE (%)		Recovery of PCE (%)	
	inner sampler	outer sampler	inner sampler	outer sampler
1	63	13	61	11
2	53	14	53	10
3	48	13	49	10

A suggested path of analyte escape is the holes through which the samplers were inserted. In order to verify this hypothesis, another experiment was performed with four samples prepared and spiked in a similar procedure as in the previous experiment. Two of the samples were exposed to inner and outer WMS inserted through holes in the caps (Figure 4-3, a), while the other two were exposed to inner and outer WMS placed inside the jars with no holes (Figure 4-3, b). The samplers in the latter scenario were held inside the jars using plastic holders (especially designed to hold them WMS) provided with four metal legs (prepared from paper clips). The samplers were retrieved after one week of exposure to be analyzed. The results are presented in Table 4-4. In this table, higher recovery of both compounds can be observed in the inner samplers that were placed inside the sample containers. On the other hand, lower amounts of analytes were detected in the outer samplers except for the amount of PCE detected in the outer sampler exposed to the first sample, which could be caused by other experimental errors.

(a) (b)

Figure 4-3: Successive sampling of analytes using internal and external WMS held (a) through holes in the caps (b) inside the sample jars without holes in the caps

Table 4-4: Results of successive sampling of the analytes using inner and outer WMS; in Samples 1 and 2 the samplers were inserted through holes in the caps of the jars, while in Samples 3 and 4 the samplers were placed inside the jars

	Sample	Recovery of TCE (%)		Recovery of PCE (%)	
		inner sampler	outer sampler	inner sampler	outer sampler
Samplers placed inside the jars	1	96	1	71	11
	2	83	7	83	2
Samplers installed through holes	3	59	19	48	11
	4	48	18	38	10

Based on these results, one can conclude that the major loss of analytes was through the hole drilled in the cover of the sample container. Thus, the experimental setup was modified for all the following experiments so that the sampler was placed inside the jar in the headspace of the soil sample, while the container was sealed with a cover containing no holes (Figure 4-4). For the rest of the experiments, glass, silane-treated containers with Teflon liner were used (Environmental Sampling Supply, Glass Wide Mouth, PC GLS, Silane Trtd, Clr Tall, 250 mL, Purchased from Delta Scientific Laboratory Products Ltd, ON). These containers were used to avoid potential adsorption of analytes to the inner surfaces.

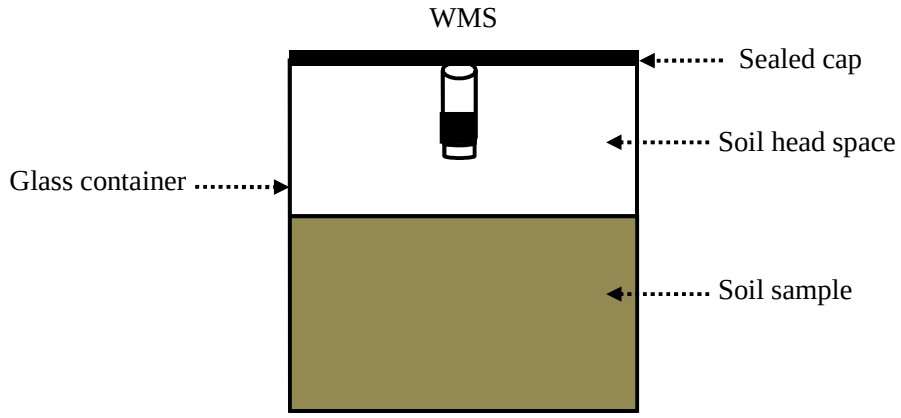

Figure 4-4: Modified setup for extracting VOCs from bulk soil using the WMS

4.2.3. Examination of the effects of different parameter on the extraction efficiency

In this part of the work, three parameters were studied: temperature, water content of the soil and the extraction time. Two-level, three-factor factorial design was used to evaluate the effects of these parameters. The levels at which the factors were studied are presented in Table 4-5.

Table 4-5: Factors studied in the experimental design and their levels

		Levels	
	Factors	+	-
Factor 1	Temperature (A) (°C)	45	25
Factor 2	Amount of water (B) (µl)	500	100
Factor 3	Exposure time (C) (days)	3	1

The 2^3 design with one replication requires a total of 16 experiments. Therefore, 16 samples of 20 g of sand were prepared. 400 µl of distilled water was added to eight of them. All samples were then spiked with a 100 µl aliquot of the aqueous solution prepared as described in Section (4.2.2.1). A WMS was placed inside each container in the same manner presented in the previous section. The containers were sealed and eight of them were left at room temperature, while the other eight were placed in the oven at 45 °C as presented in Table 4-6 considering that one replicate was performed for each experiment. The average recoveries achieved in these experiments after the assigned exposure times, as presented in Table 4-6, demonstrate high extraction efficiency from all samples (recovery ranged between 71% and 114% for TCE and between 67% and 107% for PCE).

Table 4-6: Three-factor factorial design and the average recovery of TCE and PCE from sand

Temperature (A)	**Water content (B)**	**Exposure time (C)**	**TCE average recovery (%)**	**PCE average recovery (%)**
-	-	-	109	95
+	-	-	89	86
-	+	-	71	67
+	+	-	87	80
-	-	+	75	73
+	-	+	108	105
-	+	+	114	107
+	+	+	101	95

The estimated effects were calculated using table of contrasts; the results are presented in Tables 4-7 and 4-8. Comparing the estimated effects for each factor with the standard errors for both compounds, we can see that the single-factor effects for temperature (A) and the water content (B) were smaller than two times the standard errors. The same conclusion can be reached regarding the effects of the exposure time (C) on TCE recovery, the two factor interaction between the temperature and the amount of added water (AB), and the interaction between the temperature and the exposure time (AC). However, the estimated effect of the exposure time (C) on PCE recovery and the estimated effect of the interaction between the water content and the exposure time (BC) for both compounds were higher than two times the standard errors, but lower than three times the standard errors. On the other hand, the three-factor-interaction effects are approximately equal to three times the standard errors for both analytes. That means that the effect of the exposure time depends on the water content and the extraction temperature. In other words, with higher water content, better extraction efficiency can be achieved for longer extraction time, especially at ambient temperature. However, these effects, within the limits of these experiments, were not highly significant. These effects are illustrated by the standardized Pareto charts presented in Figure 4-5 and Figure 4-6. These charts were produced using STATGRAPHICS Centurion XVI software (Version 16.1.18). In these figures, the significance limit, determined by the software, corresponds to the location of the Student's t critical value at 5% significance level [66]. These charts demonstrate significant effect of the third degree interaction between the three factors and a lower effect of the second degree interaction between the water content and the exposure time. It should be pointed out, however, that a third-degree interaction between factors is highly improbable; hence, even though the magnitude of the three-

factor-interaction effect was found to be statistically significant, it is more likely that the result was due to a combination of random factors.

Table 4-7: Estimated effects of the factors on TCE recovery from sand

	Effects	Estimated effects
	Average	94.071
Main effects	Temperature (A)	4.166
	Water added (B)	-2.155
	Exposure time (C)	10.442
Second degree interactions	AB	-2.787
	AC	5.788
	BC	17.969
Third degree interaction	ABC	-20.430

Standard error of an effect (SE) = 6.72
2 x SE (effect) = 13.44
3 x SE (effect) = 20.16

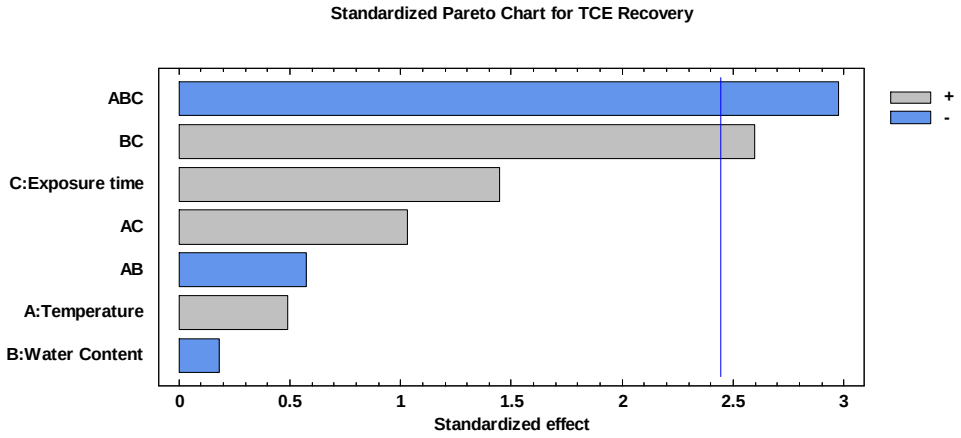

Figure 4-5: Standardized Pareto chart for PCE recovery from sand soil

Table 4-8: Estimated effects of the factors on PCE recovery from sand

	Effects	Estimated effects
	Average	88.44
Main effects	Temperature (A)	6.17
	Water added (B)	-2.45
	Exposure time (C)	12.97
Second degree interactions	AB	-5.86
	AC	4.25
	BC	14.49
Third degree interaction	ABC	-16.49

SE (effect) = 5.65

2 x SE (Effect) = 11.29

3 x SE (Effect) =16.94

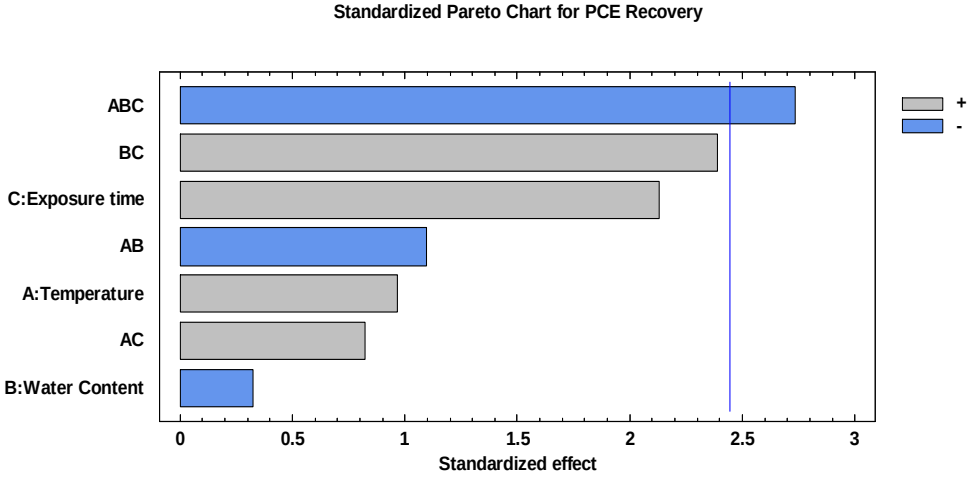

Figure 4-6: Standardized Pareto chart for PCE recovery from sand soil

The same experimental design, with the factors and levels presented in Table 4-5, was repeated to study the effects of these parameters on the extraction efficiency of TCE and PCE from another type of soil with a high organic content. A rich dark humus soil (Black Earth, Vigoro) was studied in this work. A set of 16 samples was prepared, spiked and exposed to WMS following the same procedure used with the sandy soil. The average recovery obtained in these experiments is presented in Table 4-9. As predicted, lower extraction efficiency was achieved compared to that obtained in the case of extraction from sand due to the higher absorptivity of the soil. Additionally, the extraction efficiency was enhanced at higher temperature as demonstrated in the table.

Table 4-9: Three-factor factorial design and the average recovery of TCE and PCE from Back Earth soil

Temperature (A)	Water added (B)	Exposure time (C)	TCE average recovery (%)	PCE average recovery (%)
-	-	-	12	17
+	-	-	26	35
-	+	-	14	16
+	+	-	37	43
-	-	+	8	14
+	-	+	30	50
-	+	+	15	19
+	+	+	41	56

By examining the results presented in Table 4-10 and Table 4-11, the single-factor effects for the water content (B) and the exposure time (C) were found to be smaller than two times the standard error, while the estimated effect of temperature was higher than three times

the standard error for both compounds. Therefore, it can be concluded that temperature has a significant effect on the sampling efficiency using the described method; that is, higher extraction efficiency can be achieved at higher temperature. On the other hand, all interactions of second and third degrees between factors were insignificant within the limits of these experiments. These conclusions are illustrated by Pareto charts shown in Figures 4-7 and 4-8.

Table 4-10: Estimated effects of the factors on TCE recovery from Black Earth soil

	Effects	Estimated effects
	Average	22.79
Main effects	Temperature (A)	21.13
	Water added (B)	7.74
	Exposure time (C)	1.34
Second degree interactions	AB	3.65
	AC	2.57
	CB	0.99
Third degree interaction	ABC	-1.19

SE (effect) = 4.84
2 x SE (effect) = 9.68
3 x SE (effect) = 14.52

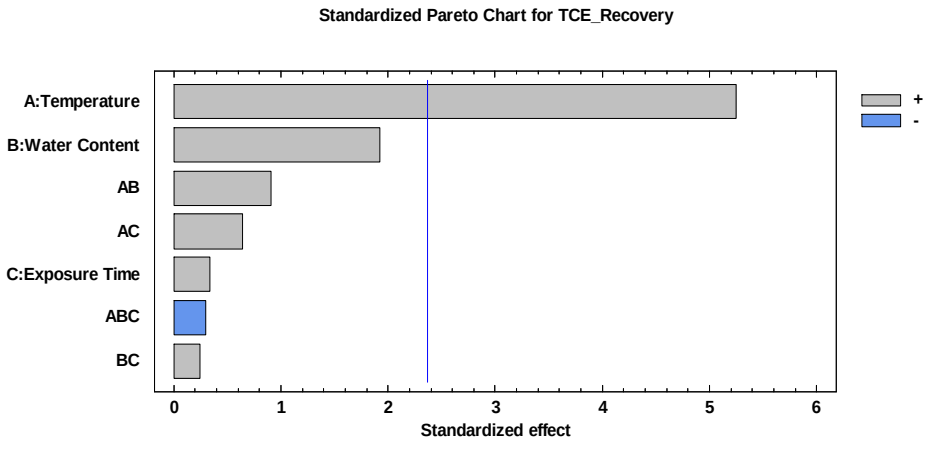

Figure 4-7: Standardized Pareto chart for TCE recovery from Black Earth soil

Table 4-11: Estimated effects of the factors on PCE recovery from Black Earth soil

	Effects	Estimated effects
	Average	31.11
Main effects	Temperature (A)	29.60
	Water added (B)	4.60
	Exposure time (C)	6.96
Second degree interactions	AB	2.81
	AC	7.04
	BC	0.82
Third degree interaction	ABC	-1.99

SE (effect) = 4.29
2 x SE (effect) = 8.59
3 x SE(effect) =12.88

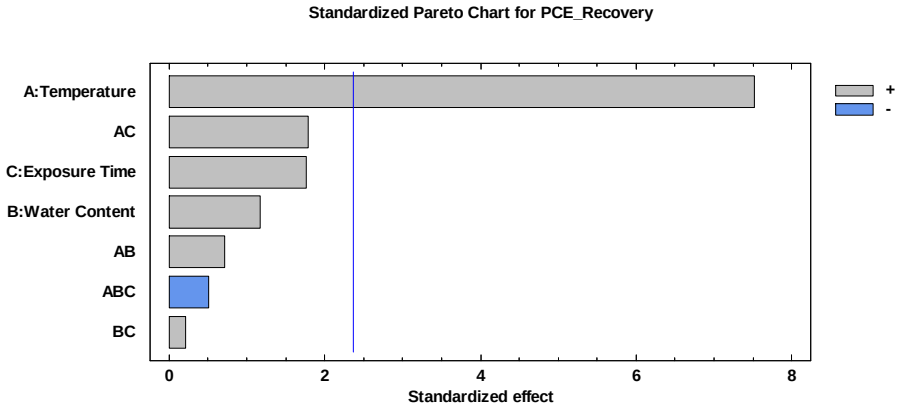

Figure 4-8: Standardized Pareto chart for PCE recovery from Black Earth soil

Further experiments were performed to examine the extraction efficiency at higher temperature. For this purpose, four experiments were performed by preparing samples of 20 g of soil (Black Earth), spiking the samples with 100 µl of an aqueous solution prepared as presented

in Section (4.2.2.1), placing the WMS inside the containers, and leaving the samples at 65 °C for one day. The results obtained from four experiments are presented in Table 4-12.

Table 4-12: Results of recoveries achieved at 65°C

Experiment	n	TCE recovery (%)	RSD %	PCE recovery (%)	RSD %
1	12	46	14.1	61	14.1
2	10	40	15.0	68	13.6
3	3	55	6.2	59	4.2
4	3	46	4.3	51	5.0
Average recovery (%)		47		60	

Compared to the recoveries achieved at 45 °C under the same conditions (26 % for TCE and 35% for PCE), the recoveries obtained at 65 °C (Table 4-12) were higher for both TCE and PCE. Furthermore, to verify that the missing portion of the analytes remained absorbed by the soil, an experiment was completed by preparing nine samples. Three soil samples were spiked with a solution prepared exactly as in the previous experiments. Three portions of similar solutions (of the same volumes and concentrations) were added to three containers with no soil. The last three containers included three 20 g soil samples spiked with 100 µl aliquots of aqueous solutions with lower concentrations. The solutions used for these three samples were prepared following the same procedure introduced in Section (4.2.2.1) with the exception of the concentrations of the methanolic solutions added to the water (~ 1 mg/ml of TCE and PCE in methanol instead of 50 mg/ml). The containers were sealed with the WMS enclosed and left at 65 °C for one day. The results of the analysis of these samples are presented in Table 4-13. It is clear from this Table that the majority of the missing portion of the analytes remained sorbed by the soil, considering that much higher recoveries were achieved from the containers with no soil; nonetheless, a small portion of the missing amounts of the analytes may have been lost during the spiking step due to the loss of few fine soil particles sticking to the syringe needle. Looking

at the recoveries obtained from the last three samples in the table, it can be observed that lower concentrations of analytes did not have a significant effect on the recoveries.

Table 4-13: Results of extraction using (a) the regular procedure in the previous experiments, (b) extraction from a solution enclosed in a container without soil, and (c) similar procedure as in (a) but at lower concentrations

Sample preparation	n	TCE recovery (%)	RSD %	PCE recovery (%)	RSD %
(a) Soil samples at ~ 180 µg/kg concentrations	3	35	9.4	51	10.4
(b) 100 µl of the spiking solution at ~ 36 µg/ml concentrations with no soil	3	87	6.7	80	6.2
(c) Soil samples spiked at ~ 3.5 µg/kg concentrations	3	43	11.2	61	18.3

4.2.4. Detection and quantification limits

The LOD and LOQ were estimated based on S/N obtained from the analysis of WMS exposed to Black Earth soil, at approximately 3.5 µg/kg concentration levels of TCE and PCE, for one day at 65 °C. An LOD as low as 0.2 µg/kg ($S/N \geq 3$) was achieved for both compounds, whereas the LOQs were 0.8 µg/kg and 0.6 µg/kg ($S/N \geq 10$) for TCE and PCE, respectively. These results reflect high sensitivity considering the nearly complete lack of sample preparation associated with this method.

4.2.5. Conclusions and recommendations

A new method of extracting VOCs from bulk soil was examined. The final setup of the method involves exposing the WMS to a freshly collected (or spiked, in this work) soil sample by placing the sampler inside the soil container, which is adequately sealed afterwards. High extraction efficiency was achieved when sampling from sand. The time of exposure was found to

increase the extraction efficiency when the water content was increased, especially at ambient temperature. A three-factor interaction effect was found to be borderline significant; however, this type of interaction is highly improbable.

When the method was tested on a soil with a higher organic content, lower extraction efficiency was achieved. The recovery was enhanced to a large extent at higher temperature with very low detection limits. The water content and the exposure time did not show significant effects within the limits of the experiments; however, more experiments are recommended to re-evaluate the effects of these factors with higher levels of water content, which better simulates real life samples. Furthermore, studying the applicability of the method on field samples is an important step towards evaluating this technique in comparison with other conventional methods.

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