UNIVERSITY OF NEUCHATEL

CENTRE FOR HYDROGEOLOGY

DEVELOPMENT OF A SYSTEM FOR *IN SITU* DETERMINATION OF CHLORINATED HYDROCARBONS IN GROUNDWATER

PhD thesis presented to the Faculty of Sciences of the University of Neuchâtel to satisfy the requirements of the degree of Doctor of Philosophy in Science

by

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Thesis Jury defense date: 4th of June 2012
Public presentation: 4th of December 2012

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Development of a system for in situ determination of chlorinated hydrocarbons in groundwater

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ACKNOWLEDGEMENTS

This project was partly funded by the Swiss Federal Office of the Environment. In the framework of this thesis, I wish gratefully to acknowledge the following persons.

I would like first of all to thank my thesis director Daniel Hunkeler who gave me the opportunity to come to Switzerland and build up this thesis. I have learnt so many things not only in the domain of analytical chemistry but also in mathematics and physics. His ability to think, try to find out solutions and his motivation for this field of research made me to be more motivated to advance. I also would like to thank Heinz Surbeck, who has a key role in this thesis as he is a member of the jury and the person who introduced me to the membrane modules. Even if he was not always in the university, he was always available to discuss with me different problems, make propositions and help me with statistical uncertainties. My special thanks to Roberto Costa who spent a lot a lot of time to help me construct this instrument, his knowledge in electronics and mechanics was very important. Also, big thanks to Hélène Demougeot for her continuous interest and advice.

I wish to express my gratitude to the members of the thesis committee, Associate Professor Mario Schirmer from the University of Neuchâtel, Lecturer Heinz Surbeck from the Swiss Federal Institute of Technology in Zurich and Professor Patrick Höhener from the University of Aix-Marseille for helping me improve this thesis after the defense.

I also would like to thank the members of the CHYN laboratory of hydrochemistry and contaminants. My special thanks to my project and office mate Pascale Ducommun who took care of me in the beginning of my life in Switzerland and she continued to be there for me at every moment, professional or private and with whom I spent many hours sharing ideas for the development of analytical methods in the lab, uncertainties and even about hydrogeological aspects. I would like also to thank especially Daniel Käser, who read my

thesis and spent a lot of time to make corrections either from a scientific point of view or for the English expressions. Really, his investment helped to improve the quality of the manuscript. I am also grateful to Florian Breider and Simon Jeannottat, the two lab mates who shared with me lab difficulties or new tricks and we passed a lot of time discussing life in the laboratory. I cannot forget the moments that we passed with all the other members of the CHYN and the ideas shared, Vivian, François G., François N., Michiel, Jaouher, Ellen, Grégoire, Alessandro, Romain, Giona, Pierik, Damian, Andrea, Julien, Guillame B., Christian, Bibiane, Jessica etc.

There are a number of people without whom this thesis would not have been finished. First of all, I want to thank my family in Greece who are far away but they are always close to me and at any occasion they show me their endless support and love. A very special thanks to my father, Antonios, that even if he is not alive, he is the one who taught me to be strong enough and to want always develop in my life. Second very special thanks to my mother; Evangellia who is always here for me and she keeps saying to me how important is to learn. Third special thanks to my brother, Achilleas for his continuous support and encouragement.

My friends in Greece showed to me the stable friendship during time despite the distance. My friends in Lausanne and Neuchâtel who supported me every time that I needed the last four years and of course my basketball team in Lausanne (BC Epalinges) for the trainings, the matches, the good and the bad moments, and the after-match aperitifs that played an important role.

Lastly, I would like to thank Clément. This thesis wouldn’t be finished without his continuous support and encouragement over this time.

Abstract

Volatile organic compounds (VOCs), and especially chlorinated hydrocarbons, are common groundwater contaminants. Efficient monitoring that can be conducted directly in the field is needed to detect a possible pollution by organic contaminants such as chlorinated hydrocarbons. The general aim of this project is to develop a portable instrument for the *in situ* measurement of chlorinated hydrocarbons in groundwater. The instrument relies on the transfer of volatile organic compounds to the gas phase followed by gas phase measurement. This research is based on three specific objectives: (a) testing of a module for extracting the contaminant from the water phase; (b) testing of a photoionization detector for gas phase analysis; and (c) calibration and evaluation of the complete instrument, including a field evaluation.

The first objective was to extract the organic contaminants from the water. For this purpose, hollow fiber membrane modules in gas stripping mode were tested. Two different membrane materials, polypropylene (PP) and poly(dimethylsiloxane) (PDMS) were tested under low gas sweep flow rates, in order to reach maximal sweep gas concentrations. Sorption to membranes and mass transfer was investigated in detail for selected chlorinated hydrocarbons such as tetrachloroethene (PCE) and trichloroethene (TCE). PCE had a greater affinity for both membranes than TCE. Mathematical formulations were developed to calculate the experimental overall mass transfer coefficients for both membranes. Using the resistance in series model, the overall mass transfer coefficient was compared to the mass transfer coefficients estimated for the different layers (water boundary layer, membrane, gaseous boundary layer). For the PDMS membrane, the limiting factor was found to be the water boundary layer. For the PP module, the mass transfer was shown to be independent of the gas flow rate. The PDMS hollow fiber module mass stripping method appeared to provide a promising way for on-line analysis for the investigated chlorinated solvents. At the selected

low gas flow rates, the PDMS hollow fiber modules yielded more stable gas phase concentrations than polypropylene modules and hence PDMS modules were used in the developed instrument.

The second objective was to evaluate a miniaturized photoionization detector (PID) for the determination of chlorinated and aromatic hydrocarbon concentrations in the gas phase. Studied compounds included the aromatic hydrocarbons: benzene, toluene, and ethylbenzene and the chlorinated hydrocarbons TCE and PCE. To test the detector performance, a series of standards with known concentrations of organic compounds were measured. The study investigated response curves, response time, linearity between response and concentration as well as the influence of gas flow rate and humidity. The laboratory tests showed that the response of the PID was linear over a concentration range of 10 to 500µg l^{-1}. The correlation coefficients R^2 varied from 0.94 to 0.99 for most of the compounds. The PID's signal was stable over time. However, the PID is showed some sensitivity to humidity, as the signal in a humidified environment was 20% lower than in a dry environment in a 50min period. However, this level of variability is acceptable for an instrument mainly developed for screening purposes.

The third objective was the evaluation of the complete system to measure chlorinated hydrocarbons in groundwater. The system involved pumping water through a PDMS hollow fiber membrane module with a surface area of 0.001m^2 at one side and passing air at the other side and monitoring the effluent air with the PID. The water and gas flow rates were 50ml min^{-1} and 12 ml min^{-1}, respectively. The extraction and detection of TCE, PCE and *cis*-dichloroethylene were (*cis*-DCE) studied experimentally for various concentrations. Field measurements were compared to conventional laboratory data obtained by gas chromatography. Only the total chlorinated hydrocarbons concentration can be determined using the miniaturized PID. This device was

capable of detecting minimum total aqueous concentration of 20μg l^{-1}. The Swiss legal limits according to OSites that apply downgradient of contaminated sites are 70μg l^{-1} for TCE and 40μg l^{-1} for PCE. These features demonstrate that the combination of the PDMS hollow fiber membrane module with the PID is feasible for semi-continuous monitoring of chlorinated solvents in groundwater.

To further test the applicability of the instrument under field conditions, a field study was carried out over a 5-month period in the contaminated military area of Lyss in Bern, Switzerland. Results showed a correlation between two methods (portable instrument and laboratory measurement through gas chromatography) with correlation coefficients (R^2) of 0.62-0.75. In general, the portable detector's concentrations are lower than the laboratory concentrations even if the regular calibration of the portable device. This is mainly because of the lower temperature of the field measurements where the Henry's coefficient is lower and consequently a lower concentration is measured in the field. Correlation coefficients are improved (R^2 equal to 0.85-0.99) when the effect of the temperature dependence of the Henry's coefficient is taken into account for points where the VC concentration is not important. Field and laboratory concentrations show a better agreement but still there are variations between the two measurements. In its current form, the prototype enables the distinction between high-, medium- and low- or non-contaminated points. It is a simple screening method for site characterization and risk assessment. The total cost of the instrument is estimated at 10.000 Swiss francs.

In conclusion, this study describes the development and demonstrates the applicability of a portable dissolved VOC detector as a screening tool. The instrument is flexible and a relatively large number of points can be measured in a relatively short period of time, while the data are available directly in the field. Limitations of instrument are the analysis of the organic compounds as a composite index, the long stabilization time and the memory effects

of the hollow fiber. So, further experiments should be considered to overcome these limitations. The use of another detector could be a possibility to detect the organic compounds individually and not as a composite index. Moreover, a heating chamber for the hollow fiber can be used with a parallel air circulation in order to accelerate the desorption of the molecules from the membrane. Finally, a possible commercial production of this device should be considered.

Keywords: on-site monitoring, portable instrument, chlorinated hydrocarbons, groundwater analysis, contamination

Résumé

Les composés organiques volatils (COV) et en particulier les hydrocarbures chlorés sont des contaminants des eaux souterraines. Un « monitoring » peut être effectué directement sur le terrain afin de faire un « screening » rapide et observer une éventuelle pollution par les hydrocarbures chlorés et / ou déterminer les options de traitement dans le cas d'une contamination. L'objectif principal de ce projet est de développer un instrument portable pour mesurer *in situ* des hydrocarbures chlorés dans les eaux souterraines. Cette recherche est basée sur trois objectifs: (a) l'essai d'un module pour extraire des contaminants de la phase aqueuse à la phase gazeuse, (b) l'essai d'un détecteur de photoionisation (PID) pour l'analyse de la phase gazeuse et (c) l'étalonnage et l'évaluation de l'instrument complet, comprenant des mesures de terrain.

Le premier objectif était d'extraire les contaminants organiques de l'eau. Dans ce but, les modules à membrane en fibres combinées avec la méthode de décapage de gaz à membrane ont été testés comme un outil analytique pour mesurer en ligne les solvants chlorés dans des échantillons aqueux. L'avantage de cette méthodologie est l'utilisation de ces modules à membrane; c'est une méthode simple, rapide, sensible et une technologie « sans solvant ». De plus, l'analyse des échantillons aqueux se fait directement sur le terrain et ne demande que peu de temps. Deux différents matériaux de membrane, polypropylène (PP) et poly(dimethylsiloxane) (PDMS) ont été testés avec des débits de gaz faibles, afin d'obtenir des concentrations gazeuses maximales. Deux types des solvants chlorés ont été choisis, le trichloroéthylène (TCE) et le tetrachloroéthylène (PCE), pour l'évaluation du système. Les résultats montrent une meilleure interprétation de l'extraction des composants organiques avec du PDMS dans la phase gazeuse que celle avec la fibre PP. Elle rend l'analyse en ligne possible grâce à des détecteurs de gaz ou à la chromatographie en phase gazeuse. La diffusion des composés à travers la membrane suit la loi de Fick et, dans des conditions d'équilibre, la

concentration dans la phase gazeuse est en relation avec celle de l'eau d'après la loi de Henry. La sorption de chaque composé sur la membrane a été déterminée expérimentalement. Le PCE a présenté une plus grande affinité pour les deux membranes que le TCE. Des formules mathématiques ont été développées pour calculer les coefficients globaux de transfert de masse pour les deux membranes en utilisant des valeurs expérimentales. Pour le module PDMS, la couche de la phase aqueuse est le facteur qui domine le processus. Celle-ci dépend indirectement du débit de gaz et se réduit lors d'un flux de gaz plus rapide. Pour le module PP, les résultats ont montré que le transfert de masse est indépendant du débit de gaz. L'utilisation du module à membrane en fibres PDMS avec la méthode de décapage de gaz à membrane serait une voie prometteuse pour l'analyse en ligne des solvants chlorés testés dans cette étude.

Le deuxième objectif, après le transfert des composants de la phase aqueuse en gazeuse, était l'évaluation d'un détecteur de photoionisation miniaturisé pour l'analyse de la phase gazeuse. Les composés testés sont des hydrocarbures aromatiques, benzène, toluène, éthylbenzène et des hydrocarbures chlorés (TCE, PCE). Pour évaluer la performance du détecteur, une série des standards avec des concentrations connues ont été mesurés. Cette comparaison est basée sur les mesures du détecteur PID et une mesure parallèle obtenue par chromatographie gazeuse. L'étude a examiné les courbes de réponse, le temps de réponse, la linéarité entre la réponse et la concentration et l'influence du débit de gaz et de l'humidité. La réponse du détecteur PID était linéaire pour une gamme des concentrations de 10 à 500μg l^{-1} and les coefficients de corrélation variaient de 0.94 à 0.99 pour la plupart de composés. Le signal du détecteur était stable dans le temps. Une sensibilité à l'humidité était présente car le signal après 50min dans un environnement humidifié était 20% inférieur du signal dans un environnement non-humidifié. Le PID est une bonne option pour la mesure des composés organiques dans la phase gazeuse. Le troisième objectif était l'évaluation du système complet

de mesure des hydrocarbures chlorés dans les eaux souterraines. Tout d'abord, l'eau a été pompée d'un côté du module à membrane et, de l'autre côté, un débit de gaz a été appliqué. Le gaz effluent a été surveillé avec le PID. Les débits de l'eau et du gaz ont été à 50ml min^{-1} et 12 ml min^{-1}, respectivement. L'extraction et la détection du TCE, PCE et *cis*-dichloroéthylène (*cis*-DCE) ont été étudiées expérimentalement pour de concentrations différentes. Une comparaison des mesures entre les valeurs du terrain et celles obtenues par des données du laboratoire a été effectuée. Seule la concentration totale des solvants chlorés peut être déterminée en utilisant le détecteur PID. La concentration minimale dans l'eau que cet instrument peut détecter est 20µg l^{-1}. Les valeurs limites du TCE et PCE dans les eaux souterraines en Suisse sont respectivement de 70µg l^{-1} et 40µg l^{-1} pour les sites contaminés. Ces caractéristiques montrent que la combinaison du module à membrane avec un détecteur PID peut être utilisée pour un « monitoring » des solvants chlorés dans les eaux souterraines.

Le détecteur portable de COV dissous permettrait potentiellement de « monitorer » la contamination. Une étude de terrain a donc été réalisée sur une période de 5 mois dans la zone militaire de Lyss dans le canton de Berne, en Suisse. Les résultats ont montré une corrélation entre les deux méthodes (les mesures avec l'instrument portable et celles de laboratoire par chromatographie en phase gazeuse) avec des coefficients de corrélation (R^2) de 0.62 à 0.75. Les concentrations mesurées avec l'instrument portable sont, de manière générale, plus faibles que les concentrations de laboratoire même si l'instrument a régulièrement été calibré. Ceci est expliqué par une température inférieure lors des mesures de terrain. Le coefficient de Henry est plus faible et par conséquent une concentration plus basse est mesurée dans le domaine. Les coefficients de corrélation se sont améliorés (0.85-0.92) lorsque cet effet a été pris en compte pour les points quand la concentration du chlorure de vinyle (VC) était faible ou inexistante. Les valeurs des concentrations entre les deux mesures ont été approchées mais

des variations sont toujours présentes. Dans sa forme actuelle, le prototype permet la distinction entre les points de haute, de moyenne et de basse ou non contamination.

En conclusion, cette étude décrit le développement d'un détecteur portable de COV dissous et démontre son applicabilité comme un appareil de « screening ». L'instrument permet une souplesse d'utilisation. Un nombre relativement important de points peuvent être mesurés sur une courte période de temps, tandis que les données sont disponibles directement sur le terrain. L'analyse des composés sous la forme d'une concentration totale, la longue stabilisation et l'effet de mémoire de la membrane sont des restrictions du système. Cependant, des expériences futures devraient être prises en considération afin d'envisager une éventuelle production commerciale de ce dispositif. En outre, une chambre de chauffage au tour de la membrane peut être utilisée en parallèle avec une circulation d'air afin d'accélérer la désorption des molécules de la membrane.

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List of Abbreviations

1/K	overall mass transfer resistance
A	area across which the diffusion takes place
C_g	concentration in the gas phase
$C_{g,eq}$	expected equilibrium gas phase concentration
$C_{g,in}$	gas concentration at the feed side of the membrane
$C_{g,out}$	gas concentration outside the membrane
$C_{g,z}$	gas concentration at distance *z* from the inlet of the hollow fiber
cis-DCE	*cis*-dichloroethylene
C_m	membrane concentration
$C_{m,in}$	membrane concentration at the feed side of the membrane at the liquid side
$C_{m,out}$	membrane concentration at the outside of the membrane at the gas side
C_o	concentration of the gas standard
C_w	bulk water concentration
$C_{w,in}$	water influent concentration
$C_{w,out}$	water effluent concentration
$C_{w,z}^{eq}$	water phase concentration that would be in equilibrium with the bulk gas phase concentration at distance z from the inlet of the hollow fiber
C_{wg}	water concentration in equilibrium with the gas concentration at the feed side of the membrane
d	thickness of the membrane
D	diffusion coefficient
d_e	equivalent diameter of the shell
D_g	diffusion coeficient in the gas phase
d_i	inner diameter of the fiber
D_m	diffusion coefficient through the membrane
DNAPLs	dense non- aqueous phase liquids
d_o	outer diameter of the fiber
D_w	diffusion coefficient in the water phase
ECD	electron conductivity detector
EICD	electrolytic conductivity detector
f	function of geometry
F	mass flux across the membrane
FID	flame ionization detector
GC	gas chromatography
Gz	Graetz numbe
H	Henry's coefficient
IMS	Ion mobility spectrometry
K	overall mass transfer coefficient
K_d	membrane-water partition coefficient
k_g	gas phase mass transfer coefficient
k_m	membrane mass transfer coefficient
K_{OC}	soil organic carbon - water partition coefficient
K_p	gas-membrane distribution coefficient
k_w	water mass transfer coefficient
L	length of the membrane
MIP	membrane interface probe
MIR	mid-infrared spectra range
M_m	membrane mass

MS	mass spectrometry
MTBE	methyl-tert-butyl-ether
MW	molecular weight
N	number of fibers
NIR	near infrared spectra range
P&T	purge-and-trap
p^*_i	vapour pressure
PCE	tetrachloroethylene
PDMS	poly(dimethylsiloxane)
PID	photoionization detector
PP	polypropylene
PTFE	polytetrafluoroethylene
PVC	polyvinyl chloride
q	flow rate
Q_g	gas flow rate
Q_w	water flow rate
R	ideal gas constant
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
S_i	inner diameter of the shell unit
SPME	solid phase microextraction
t	time
T	temperature
TCE	trichloroethylene
u_g	gas velocity
u_w	water velocity
V	volume
VC	vinyl chloride
v_g	gas viscosity
V_g	gas volume
VOC	volatile organic compound
z	distance from the hollow fiber inlet
α	surface to volume ratio
ΔC	drop between the effluent and influent aqueous concentration
ΔM	amount sorbed on the membrane
Δt	time interval
Δx	gas boundary layer thickness
μ	viscosity
ρ	density

CHAPTER 1

INTRODUCTION

1.1. GENERAL BACKGROUND

Volatile organic compounds (VOC) contamination is a widespread environmental problem. Compounds, such as trichloroethylene (TCE) and tetrachloroethylene (PCE), also referred to as dense non-aqueous phase liquids (DNAPLs), were used extensively in degreasing and equipment cleaning operations in the past, with disposal practices that led to their release to the environment. Contamination of water supplies by VOCs is a common problem (Clark et al., 1984). An estimated 1.6 to 5.0 million tons of VOCs enters the environment every year (Shen and Sewell, 1988), thus causing a significant pollution burden. Contamination sources include the following: hazardous waste disposal sites, improper disposal of common industrial solvents, leaking storage tanks, municipal industrial landfills, septic tanks, use of highly toxic pesticides and accidental spills, etc. Many of these substances are toxic; some are considered to be carcinogenic, mutagenic or teratogenic.

The presence of dangerous substances in the aquatic environment necessitates the careful and systematic control of its state. More specifically, groundwater is one of the most valuable natural resources. It has many uses, and most importantly it is a drinking water supply. In rural areas, in particular, domestic water needs are commonly met by groundwater resources. Additionally the quantity of the useable groundwater in any given area is linked to the quality of the water available for various uses. Groundwater monitoring serves a number of roles in the characterization and remediation of contaminated groundwater. During characterization processes, groundwater is analyzed to determine the type of contamination as well as its horizontal and vertical extent. The analytical data obtained can help to choose the remedial

approach. Once the remediation process is applied, groundwater monitoring is used to follow the progress and the efficiency. Moreover, data can be obtained from wells within a plume to define the progress toward aquifer restoration and outside of the plume to ensure that contaminants are not migrating toward potential receptors. Also, data from actual receptors, as supply wells or surface water, can give the information if contamination has reached them.

1.2. DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOCs) IN GROUNDWATER

The determination of specific volatile organic compounds (VOCs) in groundwater is an important analytical problem. The traditional method for analysis of volatile organic priority pollutants involves obtaining water samples from the field, transporting them to the laboratory and analyzing them by a specific procedure.

The collection, preparation and analysis of the samples are critical steps in every analytical procedure. Concepts for a proper sample collection have been widely discussed in books and publications (Kuran and Sojak, 1996; Lawrence, 1991; Stroomberg et al.; Pawliszyn; Chiavarini et al., 1991; Pawliszyn, 2003; Huybrecths et al., 2003; Rawa-Adkonis et al., 2003; Biziuk and Przyjazny, 1996). Considering the volatility and the tendency to sorb of the compounds being determined, the collection, preparation and analysis of the water samples for VOC determination requires particular attention. The basic problem is preserving the representative character of the collected water sample to be analyzed in the laboratory. Factors that influence the composition of the collected water can be separated in two categories, positive and negative deviations. Positive deviations, as a result of sample contamination, include absorption of volatile organic compounds from the air in the laboratory, contamination of the sample with the reagents used in trace analysis (including pure water), secondary contamination of the sample with components of the mixtures for washing laboratory wares, used at different stages of analytical procedures, changes in the

composition of standard solutions during their storage, contact of the analyzed sample with contaminated containers or analytical instruments, and contamination as the result of desorption from the container walls (memory effect), and introduction of the contaminants by the analyst himself.

Negative deviations include the loss of volatile compounds from the analyzed samples as a results of liberating (by evaporation, permeation, diffusion) the volatile components during the collection, transport and storage of water samples (e.g., each opening of the container in order to get a sample for analysis may cause the loss of the volatile analytes) and other operations connected with handling the sample, adsorption of analyzed compounds on the walls and caps of the containers and instruments used for analysis, and changes in the composition of the sample during storage as the result of such processes as chemical degradation, biodegradation, hydrolysis, oxidation reduction, etc.

The most frequently used analytical technique for determining the concentrations of organic compounds in water is a gas chromatographer (GC) equipped with an appropriate detector. Volatile organic compounds (VOCs) in environmental samples may exist as complex mixtures and/or at very low concentrations (ppt to ppb range). Subsequently, the GC technique must be supplemented by some method for sample preconcentration.

Gas ‘purging and trapping’ is the generally accepted method for isolation, concentration, and determination of volatile organic compounds in water samples(EPA SW-846 Method 8260B; Reding, 1987; Wylie, 1988). This method is used with almost any GC detector –MS, FID, ECD, and electrolytic conductivity detector (EICD). There are other common techniques for the isolation of volatile organic compounds from water samples, like headspace analysis(Lesage and Brown, 1994; Cammann and Hubner, 1993; Safarova et al., 2004; Foerst et al., 1989; Herzfeld et al., 1989; Dills et al., 1991; Namiesnik et al., 1984; Kolb et al., 1994; Maris et al., 1999; Farajzadeh and Mardani, 2001; Naddaf and Balla, 2000; Vitenberg, 1991;

Snow and Slack, 2002; Kolb, 1999; Kuivinen and Johnsson, 1999), distillation techniques(Clark et al., 1984; Poole et al., 1990; Kozloski, 1985; Murray, 1979), liquid extraction techniques(Namiesnik et al., 1990; Poole et al., 1990; Geissler and Scholer, 1991; Golfinopoulos et al., 2001; Zoccolillo and Rellori, 1994; Harrison et al., 1994), solid or stationary phase extraction techniques (Liska, 2000; Baltussen et al., 2002; Namiesnik et al., 1984; Baltussen et al., 1999; Wennrich et al., 2001; Popp et al., 2001; Kolahgar et al., 2002; Sandra et al., 2001 ; Blasco et al., 2002; Arthur and Pawliszyn, 1990) and membrane extraction techniques(Aoki and Kawakami, 1992; Yang and Pawliszyn, 1993; Hauser et al., 2001; Hauser and Popp, 2001; Matz et al., 1999; Jonsson and Mathiasson, 1999; Jonsson and Mathiasson, 2001; Jonsson and Mathiasson, 2000; Van de Merbel, 1999)

Conventional methods for analysis of VOCs in aqueous matrix have their merits and limitations, and are mostly used for laboratory analysis. Whilst they are extremely versatile, sensitive and selective, they are expensive and labor-intensive, thus limiting the frequency of data collection. In addition, the collection, preparation and transportation of the samples from the monitoring wells to the laboratory are factors that can influence the results of the groundwater analysis. The large number of samples collected and analyzed every year, the high cost of this procedure and the potential errors in the results are all limitations that call for an improvement of such groundwater monitoring techniques.

We hypothesize that the development of suitable instrumentation to facilitate analysis directly at the site under investigation is a complementary approach to the common practice which involves taking a sample, transporting it to a laboratory and then performing analysis. This is known as on-site analysis.

A number of technologies are currently being developed for *in situ* sampling and analysis of VOCs in groundwater. Some of them have been developed to collect and analyze the sample within a well, and others to automatically collect a sample, transport it out of the well and

analyze it in an instrument installed outside of the well. For example, an *in situ* chemiresistor sensor, described by Ho and Hughes (2002), has been commercialized for VOC detection. It is based on a polymer-based microsensor which has however a low sensitivity (Ho and Hughes, 2002). This system is used to estimate the contamination by providing real time *in situ* monitoring (Ho and Hughes, 2002). Another example is the membrane interface probe (MIP), developed by *Geoprobe Systems*™ to monitor VOC, which is widely used. The MIP is driven into the ground, a permeable membrane benefits to collect a gas VOC sample, which is captured and transported to the surface where analysis are conducted with an ion-trap mass spectrometer (Costanza and Davis, 2000). This system was able to provide an evaluation of a subsurface contamination in saturated soils, based on 146 *in situ* measurements made at 13 locations over a two-day campaign (Costanza and Davis, 2000). This device, however, is more suitable for soil contamination than for groundwater contamination as the cone penetrometer sensor is used for vapour analysis only. Another technology for VOC detection in the field of soil gas monitoring applications is the ion mobility spectrometry (IMS) which is based on the ionization of the contaminant in the gas phase(Morgos et al., 2010). On-site analysis performed with this instrument is very rapid. It needs 3s for each measurement, and gives comparable results with a GC-MS analysis in an EPA-certified laboratory. These last years spectrophotometric techniques have been introduced for hydrocarbon monitoring based on evanescent field absorption with optical fibers as the sensing elements either work in the near –infrared (NIR) (Buerck et al., 1994; Buerck et al., 2001; Conzen and Burck, 1993) or in the mid-infrared (MIR) spectral range (Buerck et al., 1992). The extraction of hydrocarbons from water is done through a polymer fiber, following a method that is similar to the solid-phase microextraction (SPME). Hydrocarbon species are then measured by an absorptiometric system, a spectrometer or photometer unit. These techniques demonstrate the feasibility of *in situ* monitoring at contaminated sites by providing direct quantitative data.

They provide selectivity and sensitivity but are not yet so cost-effective. An alternative detection of chemicals from an aqueous solution is the wave-guides, which are used to determine contaminant concentration (Lavers et al., 2000). The presence of contaminants changes the refractive index (an optical property) of a test strip while the reference strip is unaffected. The test and reference strip is the wave guide.

The presented technologies demonstrate the feasibility of VOC detection directly in the field. Instruments have already been developed and some of them are commercialized too and can be applied to water samples directly to the well or at the well head. However, they are often fairly complex to apply, very expensive or still at a research stage. Hence, there is a need of alternative instruments. There is an increasing number of portable devices for VOC detection, but they often require an extraction step before the sample introduction. There is also a lack of simple extraction methods to couple these instruments directly to water for continuous unattended measurement.

VOC detection technique	Limit of detection
Chemiresistor sensor	1000µg l^{-1} (aqueous concentration) for TCE
MIP Geoprobe System	5 mg l^{-1} for chlorinated solvents with a PID
Ion Mobility Spectrometry	0.58µg l^{-1} per volume for chloromethane
Mid-infrared Fiberoptic sensors	100µg l^{-1} for various VOCs (including TCE and PCE)
Wave-guides	100µg l^{-1}

Table 1.1 Comparative table of different VOC detection techniques and detection limits (References are given in the text)

1.3. OBJECTIVES OF THE RESEARCH

The main objective of this research is to develop and test a reliable instrument for the *in situ* measurement of VOC concentrations in groundwater. The underlying analytical method must be cost-effective, simple and rapid. The device should be applicable in field conditions, enable a large number of measurements in space and time, and be readily moveable from well to well. It should provide real time measurements of subsurface VOC contamination and combine in a single procedure groundwater sampling and detection of chlorinated solvents. The main purpose is to develop a semi-quantitative screening tool that can be helpful to select samples that should be send with priority for laboratory analysis for a more detailed and precise characterization. For this purpose, the developed instrument relies on two distinct processes: (1) the transfer of VOCs from the aqueous phase to the gas phase using permeable membranes; and (2) the measurement of VOC concentrations in the gas phase through a miniaturized photoionization detector (PID).

During the first step, VOCs are transferred from the water to the gas phase via membrane modules, which have the advantage of providing a large surface area for VOC exchange. The concept of using membrane modules to bring two phases into contact is not new. A typical use of these devices is the removal or dissolution of gases in the water (Membrana, technical

paper). Since the hollow fiber membranes are hydrophobic, the membrane will not allow liquid water to pass through to the gas side of the membrane. The membrane essentially acts as a support between the gas and liquid phases that allows them to interface. At this stage, the specific objective is to determine whether it is possible to use membrane modules for the extraction of VOCs for analysis.

During the second step, gas phase detection, VOCs can be determined through any gas detector and/or gas chromatography (GC) methods. For general surveying and site investigation, several recent instruments detect and determine VOCs in the gas phase at low concentrations by using a PID detector. In this research a PID is also selected, due to the high sensitivity of the instrument, which should lead to low detection limits and data availability at high temporal resolution, thereby giving the advantage of testing the performance of the system. Another advantage of that type of detector is its efficiency and its inexpensiveness. Moreover, it is capable of giving instantaneous readings and monitoring continuously. The detector responds to most vapors that have an ionization potential less than or equal to that supplied by the ionization source.

The research includes laboratory-and-field scale investigations to quantify chlorinated solvent concentrations in groundwater. Specifically, the applicability of the instrument is examined in groundwater wells at a military area of Lyss (canton of Bern), which is a VOC contaminated site. Specific objectives and study methods of individual chapters are summarized below.

Chapter 2 illustrates a laboratory study on the use of hollow fiber membrane contactors to extract dissolved chlorinated hydrocarbons for analysis. The theory of mass transfer in hollow fibers is presented, and the membrane gas stripping method is used for testing the transfer of the compounds from the aqueous phase to the gas phase for continuous analysis. Two different membrane materials are tested.

Chapter 3 illustrates a miniaturized photoionization detector which is tested in the laboratory for the determination of organic compounds in the vapor phase. The response, linearity, influence of the gas flow rate, and humidity are presented.

Chapter 4 contains the presentation of the combined membrane module with the PID system for field analysis of dissolved chlorinated hydrocarbons in groundwater. A detailed experimental setup is illustrated in this chapter. Its evaluation for extraction of VOCs from water in a laboratory and at field scale is discussed.

Chapter 5 contains the field application of the portable dissolved VOC detector and its comparison with conventional analytical techniques.

Chapter 6 summarizes the presented research and proposes extended research.

1.4. GENERAL INFORMATION ON MEMBRANE MODULES

The purpose of this section is to provide general information on the membrane modules and the theory of the mass transfer process through non porous membranes which is the membrane material finally used for the portable instrument using the gas stripping method.

1.4.1. Definition of membrane modules

A membrane module is a device that allows a gaseous phase and a liquid phase to come into direct contact with each other for the purpose of mass transfer between the two phases, without dispersing one phase into the other. A typical use of these devices is the removal or dissolution of gases in water (Membrana, technical paper). For the removal of dissolved gases from an aqueous stream, the modules are operated with aqueous fluid flow on one side of a hydrophobic membrane and a sweep gas/ or vacuum on the other side. Since the membranes are hydrophobic, it will not allow liquid water to pass through to the gas side of the membrane, as mentioned. The membrane essentially acts as a support between the gas and liquid phases that allows them to interface. Membrane modules are mostly fabricated with

hydrophobic hollow fibers. Generally, there are two types of hollow fibers distinguished by their structure. They are microporous and nonporous (dense) hollow fibers. The microporous membranes have pore size in the range of 200 to 3000nm with a transport of the molecules through these pores. The nonporous membranes contain non-continuous passages present in the polymer chain matrix and the transport of the molecules is based on its movement through these passages.

1.4.2. Transport across hollow fibers membranes

The transport mechanism for mass transfer across porous membranes occurs in the gas or water filled pores. In contrary for non-porous membranes, the mass transfer is best described by the solution–diffusion model which consists of five steps: (1) diffusion from the bulk aqueous solution through a liquid boundary layer to the membrane surface, (2) sorption of the molecules in the membrane, (3) diffusion through the membrane and (4) desorption of the molecules and (5) diffusion through the gas boundary layer outside the membrane (Figure 1.1). The transport rate of a compound through a membrane can be activated by various driving forces such as gradients in concentration, pressure, temperature or electrical potential. It should be noted that in this study, mass transfer relies on concentration gradients. While sorption models are usually based on thermodynamics of the component – membrane interaction, the diffusion is primarily modelled with Fick's law of diffusion. According to Fick's law the mass flux across the membrane (F) is given by:

$$F = AD\frac{(C_{m,out}-C_{m,in})}{d} = ADK_p\frac{(C_{g,out}-C_{g,in})}{d} \quad (1.1)$$

The membrane concentrations are related to the gas phase concentrations using the K_p gas-membrane distribution coefficient as:

$$K_p = \frac{K_d}{H} \quad (1.2)$$

Where K_d is the membrane-water partition coefficient and H is the Henry's coefficient given by the following equations:

$$K_d = \frac{C_m}{C_w} \tag{1.3}$$

$$H = \frac{C_g}{C_w} \tag{1.4}$$

Combination of equations 1.2, 1.3 and 1.4 gives:

$$\frac{K_d}{H} = \frac{C_m}{C_g} \tag{1.5}$$

In Equation 1.1 Where D is the diffusion coefficient of the specific compound through the membrane, A is the area across which the diffusion takes place, d is the thickness of the membrane, $C_{m,out}$ is the membrane concentration at the outside of the membrane at the gas side, $C_{m,in}$ is the membrane concentration at the feed side of the membrane where the molecules in the liquid phase are in contact with the membrane, K_p is the membrane-gas distribution coefficient and $C_{g,out}$ and $C_{g,in}$ are the gas concentration outside the membrane and the gas concentration inside of the membrane.

Substituting equation 1.3 and 1.5 into equation 1.1 gives:

$$F = AD\left(\frac{{}^{K_d}/_{H}C_{g,out} - K_d C_{w,m}}{d}\right) = ADK_d\left(\frac{{}^{C_{g,out}}/_{H} - C_{w,m}}{d}\right) \tag{1.6}$$

Or

$$F = \frac{ADK_d}{H}\left(\frac{C_{g,out} - C_{w,m}H}{d}\right) \tag{1.7}$$

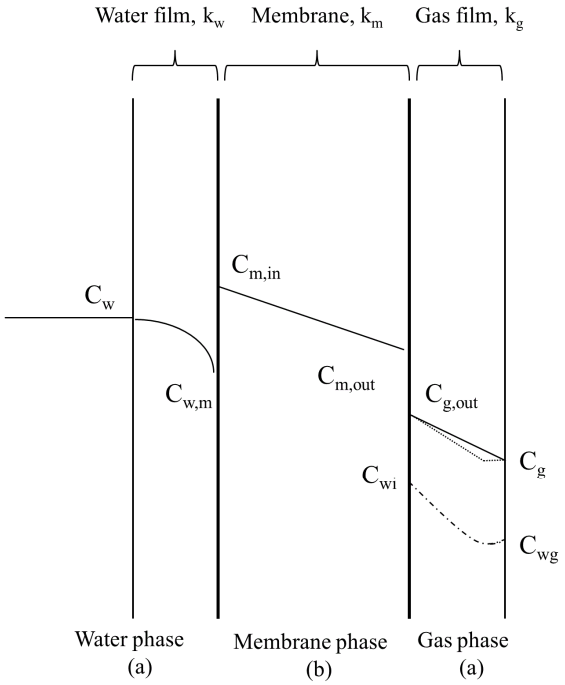

Figure 1.1 Schematic presentation of mass transfer process through a membrane where (a) are the boundary layers in water and gas phase and (b) the membrane

As the mass transfer resistance is the reciprocal of the mass transfer coefficient *K* (m/s), the overall mass transfer resistance (*1/K*) is typically expressed in a resistance in series model. For a nonporous membranes mass transfer can be described according to the solution-diffusion model as follows (Mahmud et al., 2000; Mahmud et al., 2002):

$$\frac{1}{K} = \frac{1}{k_w} + \frac{1}{K_d k_m} + \frac{1}{k_g H} \tag{1.8}$$

Where k_w is the local water phase mass transfer coefficient (m s^{-1}), k_m the membrane mass transfer coefficient (m s^{-1}) and k_g is the local gas phase mass transfer coefficient (m s^{-1}). In the membrane, the water – membrane partition coefficient K_d and in the gas phase, Henry's law coefficient *H* of the stripped compound have to be taken into account.

The mass transfer of each step, water boundary layer, membrane, gas boundary layer and the overall mass transfer based on the water phase concentration can be described by the following equations if the diffusion process is described by Fick's law:

$$F_1 = A_w k_w (C_w - C_{w,m}) \quad (1.9)$$

$$F_2 = A_m k_m (C_{m,in} - C_{m,out}) \quad (1.10)$$

$$F_3 = A_g k_g (C_{g,out} - C_g) \quad (1.11)$$

$$F_{ov} = AK (C_w - C_{wg}) \quad (1.12)$$

After entering the hollow fiber module system, molecules have to diffuse through a water boundary layer to reach the membrane. The organic molecules then partition into the membrane and diffuse through it. After leaving the membrane, the molecule diffuse through a gas boundary layer before being transported out of the module by advection.

Usually, one of the three individual mass transfer coefficients is much smaller than the two others, and the mass transfer is dominated by that phase. In many applications, the membrane resistance is the dominating factor because of the low permeability and relatively large membrane thickness. Progresses in membrane production technology and extensive research on membrane characteristics have greatly reduced the mass transfer resistance of modern membranes. In some cases, the membrane resistance is now negligible compared to the liquid phase resistance (Banat and Simandl, 1996; Juang et al., 2005). Furthermore, the gas phase resistance is often negligible for volatile compounds because the diffusion process in the gas phase is a fast process.

Correlations establishing relationship between the mass transfer coefficients and easily measurable properties of the membrane modules and operational parameters are important in the design of membrane contactors and the mass transfer coefficients can be predicted using correlations of the form (Gabelman and Hwang, 1999)

$$Sh \propto Re^{\alpha} Sc^{\beta} f(geometry) \quad (1.13)$$

Here *Sh*, *Re,* and *Sc* are the Sherwood number, the Reynolds number and the Schmidt number, respectively, and f is some function of geometry. The Sherwood number is a dimensionless number which is used in mass transfer operations. It is the ratio of convective to diffusive mass transfer and it is defined by the following equation:

$$S_h = \frac{K\,L}{D} \tag{1.14}$$

where *L* is the length of the membrane (m), *D* the diffusion coefficient ($m^2\ s^{-1}$) and *K* the mass transfer coefficient ($m\ s^{-1}$). Using dimensional analysis, the Sherwood number can further be defined as a function of the Reynolds and Schmidt numbers. The Reynolds number (dimensionless) is the ratio of inertial forces to viscous forces. The following equation defines the Reynolds number:

$$Re = \frac{d\rho v}{\mu} \tag{1.15}$$

Where *d* is the diameter of the membrane (cm), ρ is the density ($g\ ml^{-1}$), *v* is the velocity ($cm\ s^{-1}$) and μ is the viscosity ($g\ cm^{-1}\ s^{-1}$).

The Schmidt number (dimensionless) is the ratio of viscosity and mass diffusivity. It is defined by the following equation:

$$Sc = \frac{\mu}{\rho D} \tag{1.16}$$

Many authors have presented applicable correlations for both shell (outside the hollow fibers) and lumen sides (inside the hollow fibers) of the membrane module (Gabelman and Hwang, 1999; Johnson et al., 1997; Wickramasinghe et al., 1992).

CHAPTER 2

HOLLOW FIBER MEMBRANE MODULES AS AN EXTRACTION METHOD FOR DISSOLVED CHLORINATED HYDROCARBON ANALYSIS

2.1. INTRODUCTION

Membrane modules are devices that allow a gaseous phase and a liquid phase to come into direct contact with each other, for the purpose of mass transfer between the phases, without dispersing one phase into the other (Gabelman and Hwang, 1999). A typical use for these devices is the removal or dissolution of gases in water (Drioli et al., 2005). For removal of dissolved gases from an aqueous stream, membrane modules are operated with the aqueous fluid flow on one side of a hydrophobic membrane and a sweep gas applied to the other side of the membrane. Since the membrane is hydrophobic, it will not permit liquid water to pass through into the gas side of the membrane. The membrane essentially acts as a support between the gas and the liquid phases that allows them to interact. The advantage of the hollow fiber membrane modules is that they offer a high degree of compactness and a large interfacial exchange area (Gabelman and Hwang, 1999).

Membrane gas stripping, using microporous polypropylene hollow fiber membrane modules, has a great potential for the removal of volatile organic compounds (VOCs) from water (Mahmud et al., 1998). So far, several studies investigated the potential of hollow fiber membrane modules to remove VOCs from water: modules have been applied at the laboratory scale to remove chlorinated and brominated hydrocarbons (Zander et al., 1989; Semmens et al., 1989), chloroform (Mahmud et al., 2000) and toluene (Mahmud et al., 2000; Mahmud et

al., 2002; Mahmud et al., 2004), MTBE (Keller and Bierwagen, 2001) or aroma compounds (Viladomat et al., 2006)from water.

While previous studies aimed at maximizing mass transfer rates, this study explores how maximal sweep gas concentrations can be reached in view of online analysis of the sweep gas components using commonly available gas detectors or accumulation of gaseous compounds for trace analysis. In studies targeting maximal mass transfer, usually high gas flow rates are used to maintain low gas phase concentrations in the module and hence maximize the concentration gradient across the membrane (Zander et al., 1989; Mahmud et al., 2000; Mahmud et al., 2002; Mahmud et al., 2004; Keller and Bierwagen, 2001; Viladomat et al., 2006).

In this study, the effect of different gas flow rates on the sweep gas concentration is explored. In order to achieve maximized gas concentrations in the module, low gas flow rates will be tested. Ferreira et al. (2002) used a polypropylene membrane module to transfer dissolved oxygen, propane and ethanol for analysis by on-line mass spectrometry. They found a better extraction of the compounds through the module at low gas flow rates. Furthermore, the extraction can be influenced by sorption of the compounds to the membrane and sometimes with parallel swelling of the membrane (Pratt and Pawliszyn, 1992). Additional experiments on sorption are carried out as well as the membrane resistance depends on the amount of membrane water partitioning (Chapter 1, equation 1.8).

Two different membrane modules are tested; a non-porous countercurrent poly(dimethylsiloxane) (PDMS) membrane module and a microporous countercurrent polypropylene (PP) membrane module. The chlorinated solvents, trichloroethylene (TCE) and tetrachloroethylene (PCE), which are volatile, were selected.

2.1.1. Theory

In this study, where pressure is equal on both sides of the membrane, the driving force for the mass transfer in hollow fiber membrane modules from the water phase to the gas phase is a concentration gradient between the two phases. Diffusion of the compounds through the hollow fibers is assumed to follow Fick's first law as described in general in Chapter 1, with the overall flux given by:

$$F_{ov} = AK\left(C_w - C_{wg}\right) \quad (2.1)$$

Where K is the overall mass transfer coefficient (m s^{-1}), A is the area across the diffusion takes place, C_w is the bulk water concentration (µg l^{-1}) and C_{wg} the water concentration after diffusion (µg l^{-1}).

The driving force for mass transfer across the interface is proportional to the concentration difference between the phases. At near equilibrium conditions, the local concentration at distance z (from the hollow fiber inlet) of the gas phase, $C_{g,z}$, is related to the concentration in the water phase at the feed side, $C_{w,z}^{eq}$,by the dimensionless Henry's law constant H ($H=C_g/C_w$), as (Harrison and Cape, 2002; Tuner et al., 1996):

$$H = \frac{C_{g,z}}{C_{w,z}^{eq}} \quad (2.2)$$

Where $C_{g,z}$ is the concentration of the component of concern in the gas phase at distance z from the inlet of the hollow fiber and $C_{w,z}^{eq}$ is the water phase concentration that would be in equilibrium with the bulk gas phase concentration.

Theoretically in our case, the mass transfer might be limited by one or more of the following factors: (1) diffusion from the bulk aqueous solution through a liquid boundary layer to the membrane surface, (2) diffusion through the membrane under the influence of a driving force, e.g. a concentration gradient, and (3) diffusion through the gas boundary layer outside the

membrane into the stripping gas. Hence, the overall mass transfer coefficient is usually expressed for non-porous membranes as the sum of three individual resistances (Semmens et al., 1989; Mahmud et al., 2000):

$$\frac{1}{K} = \frac{1}{k_w} + \frac{1}{K_d k_m} + \frac{1}{k_g H} \tag{2.3}$$

Where k_w is the local water phase mass transfer coefficient (m s^{-1}), k_m the membrane mass transfer coefficient (m s^{-1}), k_g is the local gas phase mass transfer coefficient (m s^{-1}), K_d the water – membrane partition coefficient, and H the dimensionless coefficient (ratio of the molar concentration in the gas phase to the molar concentration in the liquid phase) of Henry's law applied to the stripped compound.

The overall mass transfer coefficient can be quantified based on the influent and effluent aqueous phase concentration described by the following equation, whose mathematical solution is presented in Appendix A:

$$K = -\frac{u_w}{(1-R)\alpha L} ln\left[\frac{C_{w,out}}{(1-R)C_{w,in}+RC_{w,out}}\right] \tag{2.4}$$

where $C_{w,in}$ and $C_{w,out}$ are the water influent and effluent concentrations, respectively, u_w is the water velocity (m s^{-1}), α is the surface to volume ratio (m^2 m^{-3}), L the hollow fiber length (m), and R is given by the following equation:

$$R = \frac{Q_w}{Q_g H} \tag{2.5}$$

where Q_w is the water flow rate (ml min^{-1}), Q_g the gas flow rate (ml min^{-1}) and H the dimensionless Henry's law coefficient.

Through Equation 2.4 applied to experimental values, it is possible to determine the overall mass transfer coefficient K.

2.2. EXPERIMENTAL

2.2.1. Materials

Hollow fiber membrane modules

Two different types of membrane modules are used: PP and PDMS. For the PDMS modules two different geometries are used, a PDMS membrane hollow fiber membrane module PermSelect^{R} PDMSXA-2500/300 (MedArray Inc., USA) and a miniaturized PDMS membrane hollow fiber membrane module PermSelect^{R} PDMSXA-10 (MedArray Inc., USA). The main characteristics of the modules are summarized in Table 2.1. For the PP module, a Celgard microporous fiber MiniModule^{R} 1.7x8.75 with polypropylene hollow fibers (Separation Products Division, Hoechst Celanese Corporation, Charlotte, NC, USA) is used. The PDMSXA-2500/300 module has a surface of 0.25m^2, the PDMSXA-10 module a surface of 0.001m^2 and the PP contactor a surface of 1m^2 surface, knitted into an array inside a housing.

	MiniModule ^{R} 1.7x8.75 PP	PermSelect^{R}PDMSXA-10	PermSelect^{R}PDMSXA-2500/300
Module length (mm)	266	130	170
Fiber O.D.(um)	300	237	237
Fiber I.D. (um)	220	167	167
Fiber length (mm)	230	39.1	110
Number of fibers	7400	32	3200
Pore size (um)	0.04	-	-
Porosity	40%	-	-
Contact area (m^2)	1	0.001	0.25
Shell side volume (ml)	132	0.443	26
Lumen side volume (ml)	73	0.398	23
Water flow inside fibers	+	-	+

Table 2.1 Hollow fiber membrane modules specifications

The housing of all modules is made of polycarbonate and the connecting tubes of PTFE (polytetrafluoroethylene). When using the PDMSXA-2500/300 module and the PP hollow fiber module, the contaminated water circulates in the lumen side (inside of the hollow fibers) while the sweep gas is applied on the shell side (outside of the hollow fibers) countercurrently. When using the PDMSXA-10 hollow fiber module, water flows over the shell side rather than within the hollow fibers because resistance of the hollow fibers to water flow is too high. The PDMSXA-2500/300 hollow fiber module was selected for the PDMS sorption experiments as the surface area is 250 times larger than that of the PDMSXA-10 module and hence sorption is easier to detect based on differences between influent and effluent concentrations. Furthermore, the shell and lumen volumes and the active surface area of the PDMSXA-2500/300 module are closer to those of the MiniModule^{R} 1.7x8.75, so the results from the sorption study are easier to compare between the two of them. For the extraction experiments the PDMSXA-10 module is used because of its smaller volume and

size, so smaller volumes of water and gas are pumped and from a practical point of view its smaller size makes its use easier in the field.

Chemicals

TCE and PCE solvents used in this study were purchased from Fluka (Switzerland). They are of analytical grade (purity ≥99.5%) and used diluted in different concentrations. Water is obtained from a Direct-Q water-purification system (Millipore S.A.S, France).

2.2.2. Experimental setup

Extraction

Aqueous solutions are prepared by injecting a concentrated water stock solution containing each target compound into deionised water at different amounts. The experimental setup is shown schematically in Fig. 2.1. Aqueous solutions are placed in 10L glass DURAN bottles. They are transferred to the housing of the module with a peristaltic pump (Ismatec SA, MCP V 5.10, Switzerland) at a flow rate of 50ml min^{-1} (±3.30%), in order to achieve a constant contact time between the water sample and the hollow fiber membrane. PTFE and Norprene® tubes (Saint-Gobain Verneret), which do not sorb VOC, are used for transferring the aqueous solution to the modules, for the sampling of aqueous samples, and for the peristaltic pump. The stripping gas is helium and the gas flow rates are adjusted by a mass flow controller (Voegtlin, red-y smart thermal mass flow controller GSC, Switzerland). The stripping gas flow rate is tested at different flow rates 3-48 ml min^{-1} (3, 6, 12, 24, 48 ml min^{-1} (±1.5%)). Experiments are conducted at atmospheric pressure. For each experiment run, the process of the mass transfer of the compounds from the water through the fibers to the gas phase is investigated. Aqueous solutions of TCE and PCE are prepared with concentrations between 600μg l^{-1} and 700μg l^{-1}. All experiments are conducted at 25^{o}C.

During the experiment, 43ml water samples are collected from the influent and effluent of the membrane module using glass syringes and dispensed in glass vials with a PTFE/silicone rubber septum.

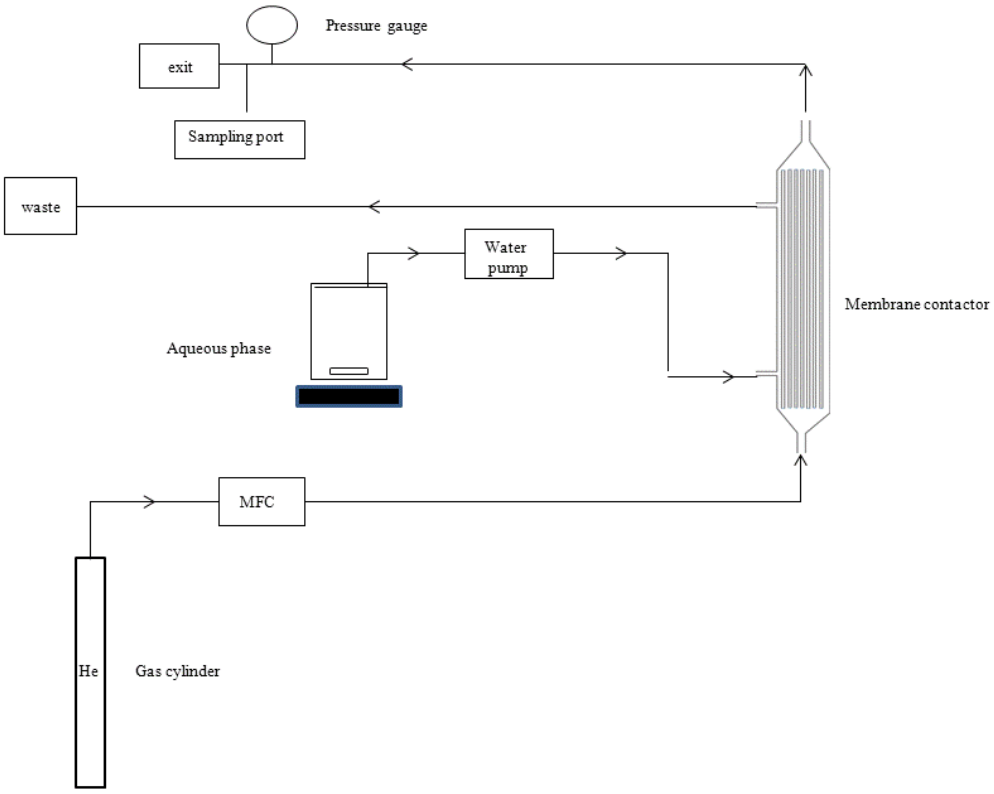

Figure 2.1 Schematic presentation of experimental setup for gas stripping in PermSelect^{R} PDMSXA-10 hollow fiber membrane module (MFC: Mass Flow Controller)

For mass balance considerations, the strip gas is sampled periodically at a sampling port at the outlet of the membrane module using gas tight syringes and the sampled gas phase is analysed by gas chromatography.

An uncertainty analysis, which was conducted by comparing each individual uncertainty of the mass transfer determinations, reveals that contributing factors are the gas concentration, the water flow rate and the gas flow rate. When these three factors are included, the estimated precision of the mass transfer coefficients calculated according to equation 2.4, is about ±9%.

Sorption

Sorption tests are conducted to determine the amount of chlorinated hydrocarbons sorbed on the polymer surface that is in contact with the feed solution. During each test, 10L of aqueous solution, with a compound concentration ranging from 600μg l^{-1} to 700μg l^{-1}, flow through the module at a rate of 50 ml min^{-1}. The gas inlet and outlet of the modules are closed with valves to avoid any gas/air circulation. Prior to the experiments, the module is free of any compound. The aqueous solution is then pumped with the peristaltic pump through the module for 2h, and water samples are collected every 10 min at the exit of the module for analysis by gas chromatography. The amount of sorption between two sampling events is calculated as follows:

$$\Delta M = Q_w \Delta C \Delta t \tag{2.6}$$

where ΔM is the amount sorbed (umol), Q_w the water flow rate (ml l^{-1}), ΔC the drop between the effluent and influent aqueous concentration (umol l^{-1}) and Δt the time interval.

Sorption is commonly quantified through the distribution coefficient K_d, which is the ratio of the sorbed phase concentration to the water phase concentration at equilibrium, referred to Chapter 1 as the membrane-water partition coefficient (Eq. 1.3). The contributing factors for the total uncertainty of the sorption are the water flow rate and the concentration, and when these two factors are included, the estimated precision of the sorption is ±7%.

When sorption occurs, the total mass removed from the water phase corresponds to:

$$M = M_m C_m + V_g C_g \tag{2.7}$$

where M_m is the membrane mass (g), C_m is the concentration in the membrane (mg g^{-1}), V_g is the volume of the gas in the shell side (ml) and C_g the concentration in the gas phase (mg ml^{-1}). At equilibrium, the membrane–water partition and Henry's law coefficients relate the concentrations as follows:

$$K_d = \frac{C_m}{C_w} \tag{2.8}$$

and

$$H = \frac{C_g}{C_w} \tag{2.9}$$

Inserting equation 2.8 and 2.9 into 2.7 yields:

$$M = M_m K_d C_w + V_g H C_w \tag{2.10}$$

Rearranging equation 2.10 gives:

$$K_d(ml/mg) = \frac{M - V_g H C_w}{M_m C_w} = \frac{M/C_w - V_g H}{M_m} = \frac{M(mg)/C_w(mg/ml) - V_g(ml)H}{M_m(mg)} \tag{2.11}$$

In its dimensionless form:

$$K_d = \frac{M - V_g H C_w}{M_m C_w} = \frac{M(mg)/C_w(mg/ml) - V_g(ml)H}{M_m(ml)} \tag{2.12}$$

Based on equation 2.12, the partition coefficient can be quantified.

2.2.3. Analytical methods

Gas chromatography

For measuring concentrations of TCE and PCE, a volume of 13ml of water is replaced by 13ml of an inert gas by injecting it to the 43ml vial with a gas tight syringe. The vials are kept in inverted position and shaken overnight at 25^{o}C to allow for phase equilibration. The headspace of the vials is sampled with VICI-Valco gas tight syringes (OMNILAB AG, Switzerland) and all gas phase samples are analysed by gas chromatography using a flame ionization detector (GC-FID, CP – 3800 Varian Inc., Creek Boulevard, CA, USA). The detector temperature is set to 250^{o}C. A BGB-5 column (30m x 0.25mm I.D., 0.50um film thickness) from BGB-Analytik (Switzerland) is used for all GC separations. The column is connected to a VICI 6port 2-position electric valve (OMNILAB AG, Switzerland) equipped

with a 250ul sample loop, for manual injection of the gas samples. The following temperature program is used: 40^{o}C for 0.50min, 40-175^{o}C at 15^{o}C min^{-1}, 175^{o}C for 3min and a column flow rate of 1.5ml min^{-1}. Calibration relies on external standards that are prepared before each experiment from a primary standard by volumetric dilution to the required concentration levels. The external standard calibration is linear over at least three orders of magnitude. The coefficients of correlation for the calibration are all higher than 0.99 for both compounds. The uncertainty (1σ) is ±3% for TCE and ±4% for PCE.

2.3. RESULTS AND DISCUSSION

2.3.1. Sorption experiments

Results from the TCE and PCE sorption tests with the PermSelect^{R} PDMSXA-2500/300 and the MiniModule^{R} 1.7x8.75 hollow fiber module are shown in figure 2.2. For the PermSelect^{R} PDMSXA-2500/300, the total amount sorbed is 15.7umol m^{-2} for TCE and 22.6umol m^{-2} for PCE, for a feed concentration of 700μg l^{-1} and of 600μg l^{-1}, respectively. With the MiniModule^{R} 1.7x8.75, the amount sorbed on the PP membrane is 7.10umol m^{-2} for TCE, and 10.23umol m^{-2} for PCE for the same feed concentrations as for the PermSelect^{R} PDMSXA-2500/300 module. PCE sorbs more strongly than TCE for comparable initial concentrations. According to Table 2.2, where calculated membrane-water partition coefficients are presented for both compounds and membrane modules, the stronger sorption of PCE into the PDMS membrane compared to TCE is consistent with the higher K_d, 204ml g^{-1} for PCE and 96ml g^{-1} for TCE. The dimensionless K_d for PCE is 197 and for TCE 92, which means that the PCE and TCE concentrations in membrane are 197 and 92 times larger than the water concentration, respectively. These values are comparable to the K_{OC} values for PCE (265ml g^{-1}) and TCE (97ml g^{-1}) provided by US EPA (1996). This tendency was expected, as K_{OC} is a measure of the partitioning of a compound between an aqueous phase and natural organic matter. The more hydrophobic the molecules are, the greater it partitions from aqueous to

organic matter. Thus the more hydrophobic PCE should sorb more on a hydrophobic membrane than the less hydrophobic TCE. Therefore, although the membrane attracts strongly both compounds, the attraction is stronger for PCE than TCE. The same observation is made for the sorption of PCE and TCE into the PP membrane, where higher PCE sorption corresponds to a higher $K_{d,}$: 51ml g^{-1} for PCE and 24ml g^{-1} for TCE. The dimensionless K_d for PCE is 49 and for TCE 22. Accordingly, the PP membrane attracts both compounds like the PDMS membrane, but the amount sorbed into the PP is lower than this one sorbed into the PDMS membrane for both compounds and so the membrane-water partition coefficients (K_d) for PP membrane are lower than for the PDMS membrane (Table 2.2). But equilibrium is not reached for both compounds and membranes and so the real K_d values will be higher than these mentioned.

According to Figure 2.2, for TCE, the sorption rate decreases over time suggesting that a sorption equilibrium is approached while for PCE only a minor decrease in the sorption rate is observed for the PDMS module while no decrease occurs for the PP module. The rate of sorption to the membrane is probably controlled by sorption-retarded diffusion into the membrane. Since TCE sorbs less, the retardation in the diffusion process is smaller, and equilibrium is approached more rapidly than for PCE, which sorbs more strongly.

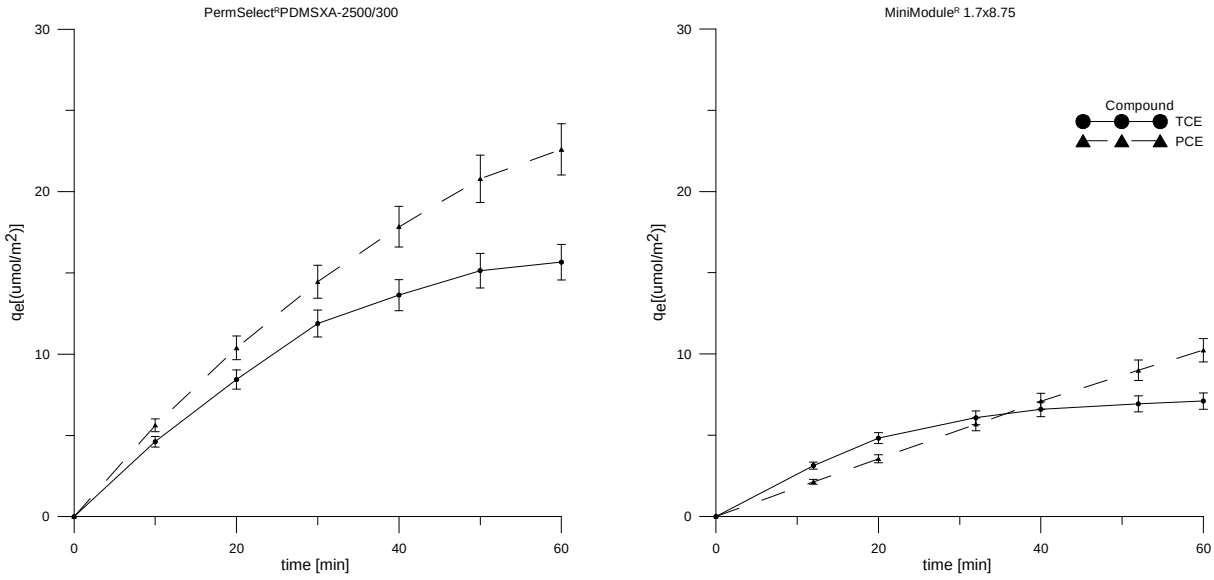

Figure 2.2 Sorption of TCE and PCE on membrane of PermSelect^R PDMSXA-2500/300 and of MiniModule^R 1.7x8.75, expressed as q_e (the ratio between the umol sorbed of each compound and the surface [m^2] of the membrane) over time. Error bars indicate experimental uncertainties.

Park et al. (2007) studied the sorption of chlorinated hydrocarbons on PDMS membrane. They indicated that compounds with more chlorine or carbon atoms sorb more strongly. Mahmud et al. (2000) found that toluene sorbed more strongly than chloroform on PP hollow fibers. The mass of each compound sorbed varied depending on the initial concentration. As in our study, the sorption increases with K_{OC}.

Membrane modules	K_d (ml g^{-1})	K_d (dimensionless)
PermSelect^R PDMSXA-2500/300		
TCE	96	92
PCE	204	197
MiniModule^R 1.7x8.75		
TCE	24	22
PCE	51	49

Table 2.2 Calculated distribution coefficients for TCE and PCE for both membrane modules

2.3.2. Extraction of TCE and PCE from aqueous solution

Figures 2.3 and 2.4 show the relative concentration $C_{g,out}/C_{g,eq}$ for different gas flow rates by using the PermSelect^R PDMSXA-10 membrane module and the MiniModule^R 1.7x8.75 membrane module, respectively. The relative concentration corresponds to the ratio between the measured gas phase concentration at the outlet of the module and the expected equilibrium gas phase concentration calculated on the basis of the inlet aqueous phase concentration using Henry's law.

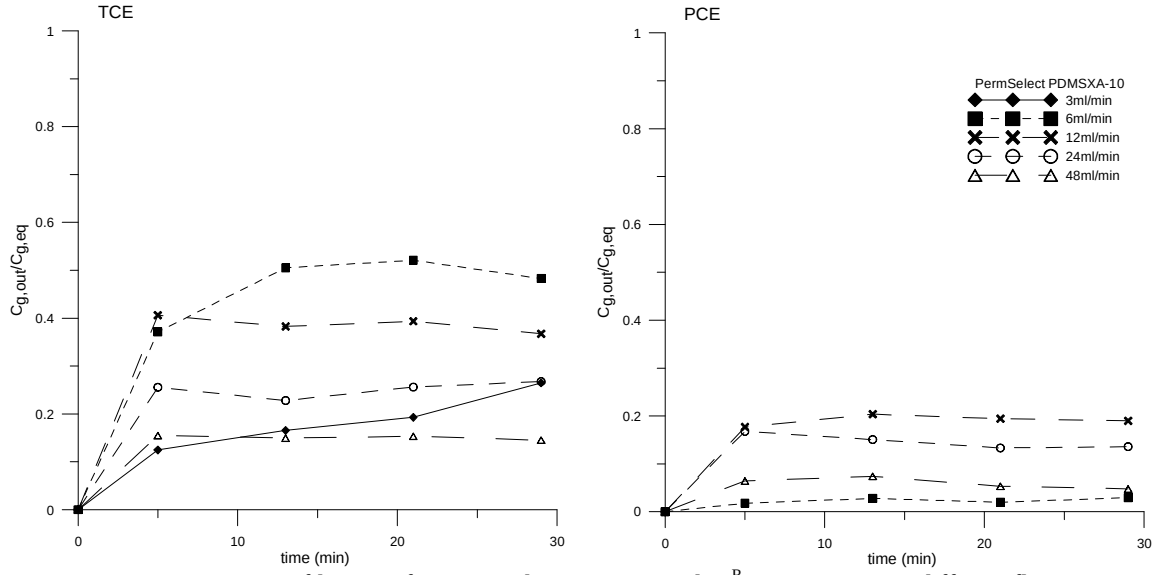

Figure 2.3 Extraction profile curve for TCE and PCE in PermSelect^R PDMSXA-10 at different flow rates

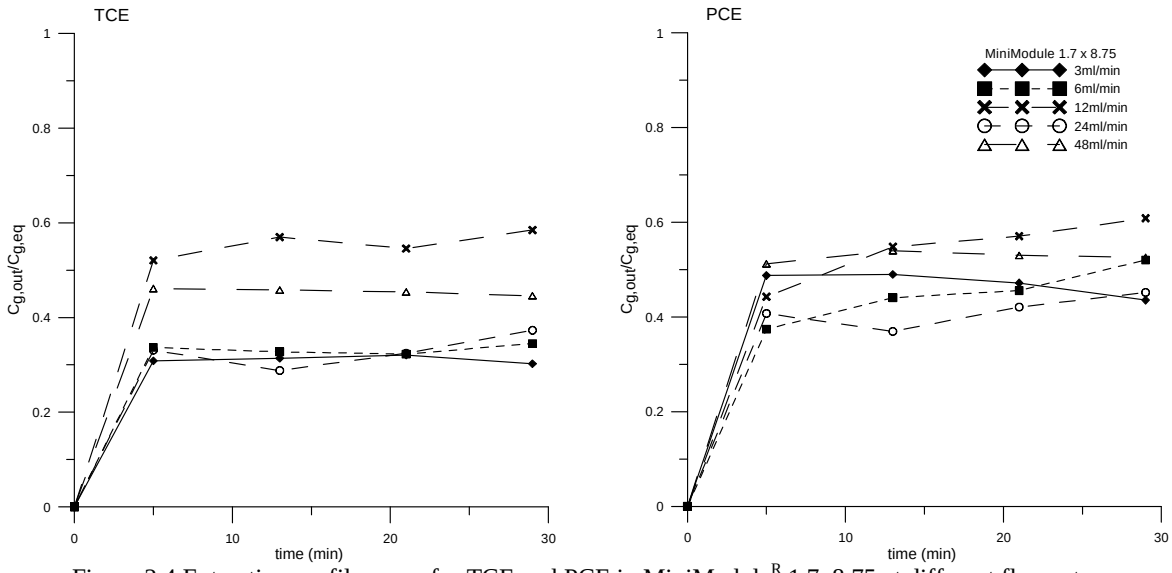

Figure 2.4 Extraction profile curve for TCE and PCE in MiniModule^R 1.7x8.75 at different flow rates

Concentrations of TCE and PCE, as a function of time and gas flow rate, are depicted in figs 2.3 and 2.4. Three main observations can be made: first, the extraction profile changes with flow rates for both modules; second the steady state is reached after 15min for both modules, except for TCE at 3ml min^{-1}; and third, the maximum extraction reaches 50% for TCE and 20% for PCE for the PDMS module, and reaches almost 50% for both TCE and PCE for the PP module.

As described through equation 2.3, the mass transfer of VOC from water to gas occurs across three layers. Considering that the diffusion coefficient in air for both compounds is 3 to 4 orders of magnitude greater than the one in water, it is expected the mass transfer coefficient in the gas phase should not control the overall process, and the gas phase boundary layer is practically negligible. The membrane should have a negligible resistance too, because the membrane is quite thin, and more specifically for membrane thickness around 100um (Keller and Bierwagen, 2001).

With respect to the PDMS module, in more quantitative manner, the overall mass transfer coefficient derived from Equation 2.4 increases slightly for both compounds with gas flow rate (Table 2.3). Overall mass transfer coefficients at 3 and 6ml min^{-1} are not reported as there is no significant difference between the two water concentrations measured at the inlet and outlet of the membrane module.

VOC	Q_w (ml min^{-1})	Q_g (ml min^{-1})	K (m s^{-1}) measured MiniModule ^{R} 1.7x8.75	K (m s^{-1}) measured PermSelect^R PDMSXA-10
TCE	50	3	-	-
		6	-	-
		12	6.90×10^{-7}	1.05×10^{-5}
		24	2.17×10^{-7}	1.67×10^{-5}
		48		1.78×10^{-5}
PCE	50	3	-	-
		6	-	-
		12	3.27×10^{-7}	9.13×10^{-6}
		24	2.12×10^{-7}	1.29×10^{-5}
		48	9.02×10^{-7}	1.24×10^{-5}

Table 2.3 Measured *K* values in the hollow fiber extraction process of VOCs at 25°C and different gas flow rates

The gas phase mass transfer coefficients given in Table 2.4 are calculated using the Sherwood number equation B.1 (Appendix B). These values, based on estimated correlations, approximate the behavior of the compounds. Within the range of gas velocities used in this study, the Sherwood correlations for estimating the gas phase mass transfer coefficients are not following Levêque's approach (equation B.1), as the overall and gas mass transfer coefficient differ in 2 order of magnitude. This can be explained by calculating the Graetz (Gz) number following equation B.2, because Levêque's approach is only applicable for Graetz number higher than 4. The Graetz number for this module ranges from 3.82×10^{-2} to 6.10×10^{-3}, values which are much lower than 4. Since the gas is flowing inside the fibers and the fiber diameter is low and the gas velocity used is low, low Graetz number values are obtained and so the Sherwood correlation used increases the gas mass transfer coefficient (Gabelman and Hwang, 1999).

According to Viladomat et al. (2006) the mass transfer coefficients inside the fibers of a membrane module for Gz lower than 6 is given by:

$$K = 0.5\ \frac{d_i u_g}{L} \tag{2.13}$$

By using this equation, the gas mass transfer coefficients are recalculated at different gas flow rates.

The recalculated gas mass transfer coefficients are given in Table 2.5. These values, based too on estimated correlation, are lower than the k_g values calculated by Levêque's approach.

To check the plausibility of the obtained gas phase mass transfer coefficients, the thickness of the boundary layer was estimated using the following equation:

$$k_g = \frac{D_g}{\Delta x} \tag{2.14}$$

Where k_g is the gas phase mass transfer coefficient (m s^{-1}), D_g is the diffusion coefficient in air (m^2 s^{-1}) and Δx the gas boundary layer thickness (m). Table 2.6 presents the estimated values of the gas boundary layer thickness at each flow rate using the recaclulated gas mass transfer coefficient values. The boundary layer thickness decreases with flow rate and the values that are quite low (2.37×10^{-4}–6.83×10^{-4}m).

VOC	Q_w (ml min^{-1})	Q_g (ml min^{-1})	k_g (m s^{-1}) calculated MiniModule ^{R} 1.7x8.75	k_g (m s^{-1}) calculated PermSelect^R PDMSXA-10
TCE	50	3	9.75×10^{-6}	1.50×10^{-2}
		6	1.86×10^{-5}	1.89×10^{-2}
		12	3.54×10^{-5}	2.38×10^{-2}
		24	6.75×10^{-5}	2.99×10^{-2}
		48	1.29×10^{-4}	3.75×10^{-2}
PCE	50	3	9.17×10^{-6}	1.41×10^{-2}
		6	1.75×10^{-5}	1.78×10^{-2}
		12	3.33×10^{-5}	2.23×10^{-2}
		24	6.35×10^{-5}	2.81×10^{-2}
		48	1.21×10^{-4}	3.53×10^{-2}

Table 2.4 Calculated kg values using Equations B.1 and B.3 (Appendix B) in the hollow fiber extraction process of VOCs at 25^{o}C and different gas flow rates

Moreover, comparing the k_g values in Table 2.4 for the PDMS module for both compounds, there is no a significant difference between TCE and PCE at each gas flow rate. This is because the values of the diffusion coefficients in air for TCE and PCE are in the same order of magnitude (FSG method, Appendix B).

VOC	Q_w (ml min^{-1})	Q_g (ml min^{-1})	k_g (m s^{-1}) recalculated PermSelect^R PDMSXA-10
TCE	50	3	1.52×10^{-4}
		6	3.05×10^{-4}
		12	6.09×10^{-4}
		24	1.22×10^{-3}
		48	2.44×10^{-3}
PCE	50	3	1.39×10^{-4}
		6	2.78×10^{-4}
		12	5.56×10^{-4}
		24	1.11×10^{-3}
		48	2.22×10^{-3}

Table 2.5 Recalculated k_g values in the PDMS hollow fiber extraction process of VOCs at 25^{o}C and different gas flow rates

VOC	Q_w (ml min^{-1})	Q_g (ml min^{-1})	Δx (m) estimated PermSelect^R PDMSXA-10
TCE	50	3	5.74×10^{-2}
		6	2.74×10^{-2}
		12	1.37×10^{-2}
		24	6.84×10^{-3}
		48	3.42×10^{-3}
PCE	50	3	5.74×10^{-2}
		6	2.74×10^{-2}
		12	1.37×10^{-24}
		24	6.84×10^{-3}
		48	3.42×10^{-3}

Table 2.6 Estimated Δx values in the hollow fiber extraction process of VOCs through the PDMS module at 25^{o}C and different gas flow rates

The membrane mass transfer coefficient can be calculated using equation B.4 (Appendix B). This coefficient depends on the compound's diffusion coefficient through the membrane and the membrane thickness, so it is independent of the gas flow rate. Dotremont et al. (1995) presented that the diffusion coefficient for TCE has mean values of 10^{-10} - 10^{-11} m^2 s^{-1}. Substituting a diffusion coefficient value of 1 x 10^{-11} m^2 s^{-1} into equation B.5, an approximate k_m of TCE is obtained with a value of 2.86 x 10^{-7} m s^{-1}. The membrane mass transfer resistance (Eq. 2.3) depends on the membrane mass transfer coefficient and the membrane – water partition coefficient. The latter (dimensionless) is equal to 92 for TCE as mentioned to Section 2.3.1. The product of these two coefficients for TCE is equal to 2.63 x 10^{-5} m s^{-1}. This means that the membrane mass resistance is lower comparing to the overall mass transfer resistance.

It is already mentioned that the overall mass transfer coefficient and the gas phase mass transfer coefficient increase slightly with gas flow rate. The recalculated gas mass transfer coefficients are higher comparing to the overall mass transfer coefficient and the gas boundary layer is low. So, the gas mass resistance is lower than the overall resistance. The membrane mass transfer coefficient is unaffected by the gas flow rate, and the membrane mass resistance is lower comparing to the overall resistance. So, among the three resistances (water, membrane and gas resistance), the water resistance is the largest. Thus diffusion through the water boundary layer controls the overall mass transfer.

As shown in Figure 2.3, the relative concentration of PCE, is almost half the one of TCE, whatever the gas flow rate. Henry's coefficient *H* determines the capacity of the gas for each compound and a given water phase concentration. The Henry coefficient for PCE is twice as large as for TCE (Table 2.7) and thus, for a given water phase concentration, the equilibrium gas phase concentration of PCE is twice as large as for TCE. Hence, if an equal amount of

PCE and TCE are transferred through the membrane, the relative concentration of PCE will only be half as large as for TCE.

VOC	H (dimensionless)	D_w (m^2 s^{-1})	D_g (m^2 s^{-1})	Solubility coefficients (mg l^{-1})
TCE	0.43	1.04×10^{-9}	8.33×10^{-6}	1.10×10^{3}
PCE	0.76	9.44×10^{-10}	7.60×10^{-6}	2×10^{2}

Table 2.7 Henry's law coefficients where $H = C_g/C_w$ (source: EPA On-line tools for Site Assessment Calculation), diffusion coefficients in water and air (FSG method) and solubility coefficient's in water (US EPA (U. S. Environmental Protection Agency). 1996. Soil Screening, Guidance) for both compounds at 25°C

Moreover, the relative concentrations of TCE and PCE decrease by increasing the gas flow rate from 6ml min^{-1} to 48ml min^{-1} for TCE, and from 12ml min^{-1} to 48ml min^{-1} for PCE. Higher gas flow rates reduces the residence time of the compounds on the module, and ultimately its concentration in the gas phase, as there is less time for the molecules to transfer from the aqueous phase to the gas phase. This does not occur for TCE at 3ml min^{-1} gas flow rate and for PCE at 6ml min^{-1} even after repetitive experiments, which cannot been explained.

Note that the greatest relative concentration is achieved at a gas flow rate of 6ml min^{-1} for TCE and of 12ml min^{-1} for PCE.

Regarding the PP module, Figure 2.4 shows the relative concentrations of the two chlorinated hydrocarbons obtained when using the MiniModule^R 1.7x8.75. With respect to this module, the overall mass transfer coefficient derived from Equation 2.4 decreases from 12ml min^{-1} to 24ml min^{-1} gas flow rate for TCE and PCE and increases from 24ml min-^{1} to 48ml min^{-1} for PCE.

The gas phase mass transfer coefficients (Table 2.4) are calculated using the Sherwood number Equation B.3 presented in Appendix B. These values as for the PDMS module are

only an approximation and it is observed that calculated values are much greater than the overall mass transfer coefficients. It should be noted that the gas flows to the shell side of the module (outside the fibers). Gabelman and Hwang (1999) presented that the mass transfer coefficient in the shell side cannot be predicted by equations based on geometry because the mass transfer coefficient does not depend on the geometry.

Taking into account the diffusion coefficient of TCE through the pores of PP membranes reported by Inguva et al. (1998) equal as 1.41 x 10^{-11} m^2 s^{-1}, the membrane mass transfer coefficient k_m can be estimated using equation B.4 (Appendix B). The k_m for TCE is equal to 3.53 x 10^{-7} m s^{-1} which is independent of the gas flow rate. The membrane mass transfer resistance (Eq. 2.3) is depending on the membrane mass transfer coefficient and the membrane – water partition coefficient. The latter (dimensionless) is equal to 22 for TCE as mentioned in Section 2.3.1. The product of these two coefficients for TCE is equal to 7.76 x 10^{-6} m s^{-1}. This means that the membrane mass resistance is low and so it should not be a limiting factor of the whole process.

The overall mass transfer coefficient decreases with the gas flow rate and the estimated gas phase mass transfer coefficients are not plausible. The membrane mass transfer coefficient is unaffected by the change of the flow rate into the gas phase. So, it is difficult to understand which factor limits the whole process.

The relative concentration of TCE decreases by increasing the gas flow rate from 12ml min^{-1} to 48 ml min^{-1} but the other three gas flow rates (3, 6, 24ml min^{-1}) do not demonstrate a clear dependence to the gas flow rate. For PCE, the relative concentrations show to be independent of the gas flow rate. This behaviour differs from the PDMS module. It should be noted that even if the conditions of the extraction experiments are the same for both modules (water and gas flow rates), the geometry and the operation conditions (lumen and shell sides) are not identical.

2.4. CONCLUSIONS

Two different hollow fiber membrane contactors are tested in this study, a PDMS hollow fiber membrane module and a microporous PP hollow fiber membrane module, in a membrane gas stripping process as an extraction method for analytical processes. Under the test conditions, the sorption phenomenon is present for both membrane modules and both compounds. PCE shows a greater affinity for both PDMS and PP membranes, due to its greater hydrophobicity.

The overall mass transfer coefficients, gas phase mass transfer coefficients and membrane mass transfer coefficients are calculated for each gas flow rate in order to determine the limiting factor of the mass transfer process. For the PDMS module, the limiting factor was found to be diffusion through the water boundary layer. Moreover, there is a decrease of the relative concentration for both compounds with an increase of the gas flow rate, as there is less time for molecules to transfer to the gas phase. For the PP module, it is difficult to understand which factor influences the mass transfer.

The mass transfer through the PermSelect^{R} PDMSXA-10 membrane module by using the gas stripping method through low gas flow rates compared to other studies where higher gas flow rates are used, is better understood, so it is chosen to be used for providing on-line measurements of chlorinated hydrocarbons in water samples.

2.6. Appendix A – Determination of *K* values

Mass balance question describing concentration changes within a hollow is given by (Mahmud et al., 1998):

$$\frac{dC}{dt} = -\frac{u_{wdC_{w,z}}}{dz} - k\alpha\left(C_{w,z} - C_{w,z}^{,eq}\right) \quad \text{(A.1)}$$

Where α is the surface to volume ratio (m^2 m^{-3}), z the distance from the hollow fiber inlet (m), C the concentration of the component of concern in the water phase at distance z and t is the time (s).

Under steady state conditions, the above relation becomes:

$$-\frac{u_w dC_{w,z}}{dz} = K\alpha\left(C_{w,z} - C_{w,z}^{eq}\right) \quad \text{(A.2)}$$

Where u_w is the liquid velocity, $C_{w,z}$ the local liquid phase concentration z from the module inlet, and $C_{w,z}^{eq}$ the liquid concentration that would be in equilibrium with the local gas phase concentration at the feed side.

We assume that the gas-liquid interface is flat, which is consistent with the hydrophobicity of the membrane surface. The assumption is practical due to the difficulties associated with measuring the contact angle in the pore. The equation (A.2) cannot be integrated to yield position dependent liquid phase concentrations, unless $C_{w,z}^{eq}$ can be expressed as a function of position or $C_{w,z}$. To do this, a macroscopic mass balance can be developed over a finite length of the module (Juang et al., 2005) from the air inlet to an arbitrary cross section at a distance z from the water inlet to obtain:

$$Q_w C_{w,z} + Q_g C_{g,in} = Q_w C_{w,out} + Q_g C_{g,z} \quad \text{(A.3)}$$

Where Q_w is the water flow rate (ml min^{-1}), Q_g the gas flow rate (ml min^{-1}) and $C_{g,in}$ and $C_{w,out}$ are the gas and water phase concentration at the gas inlet (water outlet). At z=0, C_w=$C_{w,in}$ and at z=L C_w=$C_{w,out}$ and $C_{g,z}$=$C_{g,out}$ which are the boundary conditions (Juang et al., 2005).

The concentration $C_{g,in}$ equals to zero if the influent gas in contaminant free.

$$Q_w C_{w,in} = Q_w C_{w,out} + Q_g C_{g,out} \tag{A.4}$$

or

$$C_{g,out} = \frac{Q_w}{Q_g}\left(C_{w,in} - C_{w,out}\right) \tag{A.5}$$

Substituting eq. (A.5) in Henry's law expression (Eq. 3):

$$C_{w,in}^{\text{eq}} = \frac{C_g^{eq}}{H} = \frac{\frac{Q_w}{Q_g}\left(C_{w,in} - C_{w,out}\right)}{H} = R\left(C_{w,in} - C_{w,out}\right) \tag{A.6}$$

where $R = \frac{Q_w}{Q_g H}$.

Substituting the boundary conditions and then integrating over the length of the module, the following equation can be derived:

$$\int_{C_{w,in}}^{C_{w,out}} \frac{dC_w}{\left[C_w(1-R) + RC_{w,out}\right]} = -\frac{K\alpha}{u_w} L \int_0^L dz \tag{A.7}$$

Solving Eq. (A.7) for the boundary conditions:

$$\frac{1}{1-R} ln\left|C_{w,in}(1-R) + RC_{w,out}\right|_{C_{w,in}}^{C_{w,out}} = -\frac{K\alpha}{u_w} L \tag{A.8}$$

Further solving Eq. (A.8):

$$\frac{1}{1-R} ln \frac{(1-R)C_{w,out} + RC_{w,out}}{(1-R)C_{w,in} + RC_{w,out}} = -\frac{K\alpha L}{u_w} \tag{A.9}$$

Rearranging eq. (A.9) for the overall mass transfer coefficient for a single pass through the module, the expression becomes:

$$K = -\frac{u_w}{(1-R)\alpha L} ln\left[\frac{C_{w,out}}{(1-R)C_{w,in} + RC_{w,out}}\right] \tag{A.10}$$

Parameters used for the calculations of the overall mass transfer coefficients for both compounds and modules:

Compound	TCE				
MW (g mol $^{-1}$)	131.4	131.4	131.4	131.4	131.4
$C_{w,in}$ (µg l^{-1})	610	610	610	610	610
$C_{w,out}$ (µg l^{-1})	606	593	589	575	571
Q_w (m^3 min^{-1})	$5x10^{-5}$	$5x10^{-5}$	$5x10^{-5}$	$5x10^{-5}$	$5x10^{-5}$
Q_g (m^3 min^{-1})	$3x10^{-6}$	$6x10^{-6}$	$12x10^{-6}$	$24x10^{-6}$	$48x10^{-6}$
Surface of fibers (m^2)	0.001	0.001	0.001	0.001	0.001
L (m)	0.0391	0.0391	0.0391	0.0391	0.0391
Shell side's volume (m^3)	$4.43x10^{-7}$	$4.43x10^{-7}$	$4.43x10^{-7}$	$4.43x10^{-7}$	$4.43x10^{-7}$
D_{w}Erreur ! Signet non défini. (m^2 s^{-1})	$1.04x10^{-9}$	$1.04x10^{-9}$	$1.04x10^{-9}$	$1.04x10^{-9}$	$1.04x10^{-9}$
u_w (m s^{-1})	0.0559	0.0559	0.0559	0.0559	0.0559

Table A.1. Parameters for the calculation of the overall mass transfer coefficients for the PDMS module for TCE

Compound	PCE				
MW (g mol $^{-1}$)	165.8	165.8	165.8	165.8	165.8
$C_{w,in}$ (µg l^{-1})	481	481	481	481	481
$C_{w,out}$ (µg l^{-1})	480	475	465	458	456
Q_w (m^3 min^{-1})	$5x10^{-5}$	$5x10^{-5}$	$5x10^{-5}$	$5x10^{-5}$	$5x10^{-5}$
Q_g (m^3 min^{-1})	$3x10^{-6}$	$6x10^{-6}$	$12x10^{-6}$	$24x10^{-6}$	$48x10^{-6}$
Surface of fibers (m^2)	0.001	0.001	0.001	0.001	0.001
L (m)	0.0391	0.0391	0.0391	0.0391	0.0391
Shell side's volume (m^3)	$4.43x10^{-7}$	$4.43x10^{-7}$	$4.43x10^{-7}$	$4.43x10^{-7}$	$4.43x10^{-7}$
D_w (m^2 s^{-1})	$9.45x10^{-10}$	$9.45x10^{-10}$	$9.45x10^{-10}$	$9.45x10^{-10}$	$9.45x10^{-10}$
u_w (m s^{-1})	0.0559	0.0559	0.0559	0.0559	0.0559

Table A.2. Parameters for the calculation of the overall mass transfer coefficients for the PDMS module for PCE

Compound	TCE				
MW (g mol $^{-1}$)	131.4	131.4	131.4	131.4	131.4
$C_{w,in}$ (μg l^{-1})	479	479	479	479	479
$C_{w,out}$ (μg l^{-1})	468	462	430	416	280
Q_w (m^3 min^{-1})	$5x10^{-5}$	$5x10^{-5}$	$5x10^{-5}$	$5x10^{-5}$	$5x10^{-5}$
Q_g (m^3 min^{-1})	$3x10^{-6}$	$6x10^{-6}$	$12x10^{-6}$	$24x10^{-6}$	$48x10^{-6}$
Surface of fibers (m^2)	1	1	1	1	1
L (m)	0.23	0.23	0.23	0.23	0.23
Lumen side's volume (m^3)	$7.30x10^{-5}$	$7.30x10^{-5}$	$7.30x10^{-5}$	$7.30x10^{-5}$	$7.30x10^{-5}$
D_w (m^2 s^{-1})	$1.04x10^{-9}$	$1.04x10^{-9}$	$1.04x10^{-9}$	$1.04x10^{-9}$	$1.04x10^{-9}$
u_w (m s^{-1})	0.0030	0.0030	0.0030	0.0030	0.0030

Table A.3. Parameters for the calculation of the overall mass transfer coefficients for the PP module for TCE

Compound	PCE				
MW (g mol $^{-1}$)	165.8	165.8	165.8	165.8	165.8
$C_{w,in}$ (μg l^{-1})	354	354	354	354	354
$C_{w,out}$ (μg l^{-1})	346	340	301	300	198
Q_w (m^3 min^{-1})	$5x10^{-5}$	$5x10^{-5}$	$5x10^{-5}$	$5x10^{-5}$	$5x10^{-5}$
Q_g (m^3 min^{-1})	$3x10^{-6}$	$6x10^{-6}$	$12x10^{-6}$	$24x10^{-6}$	$48x10^{-6}$
Surface of fibers (m^2)	1	1	1	1	1
L (m)	0.23	0.23	0.23	0.23	0.23
Lumen side's volume (m^3)	$7.30x10^{-5}$	$7.30x10^{-5}$	$7.30x10^{-5}$	$7.30x10^{-5}$	$7.30x10^{-5}$
D_w (m^2 s^{-1})	$9.45x10^{-10}$	$9.45x10^{-10}$	$9.45x10^{-10}$	$9.45x10^{-10}$	$9.45x10^{-10}$
u_w (m s^{-1})	0.0030	0.0030	0.0030	0.0030	0.0030

Table A.4. Parameters for the calculation of the overall mass transfer coefficients for the PP module for PCE

2.7. Appendix B – Sherwood number

As discussed in the main text, the Sherwood number is calculated for the gas mass transfer of the PermSelect^{R} PDMSXA-10 membrane contactor. To predict the lumen side mass transfer the Levêque solution is used (Gabelman and Hwang, 1999):

$$Sh = \frac{k_g d_i}{D_g} = 1.62 \left(\frac{d_i^2 u_g}{D_g L}\right)^{0.33} \quad \text{(B.1)}$$

where k_g is the gas mass transfer coefficient (m s^{-1}), d_i is inner diameter of the fiber (m), D_g is the gas diffusion coefficient for TCE and/or PCE estimated by the FSG method (method of Fuller, Schetler and Giddings) (m^2 s^{-1})(Tucker and Nelken, 1990), L the length of the fiber (m) and u_g the gas velocity (m s^{-1}).

The Graetz number is given by the following equation (Gabelman and Hwang, 1999):

$$Gz = \frac{d_i^2 u_g}{D_g L} \quad \text{(B.2)}$$

Where d_i is the inner diameter of the fiber (m), L the length of the fiber (m), u_g the gas velocity (m s^{-1}) and D_g is the gas diffusion coefficient for TCE and/or PCE estimated by the FSG method (method of Fuller, Schetler and Giddings) (m^2 s^{-1}) (Tucker and Nelken, 1990).

The following correlation is used to predict the shell side mass transfer in the MiniModule^{R} 1.7x8.75 membrane contactor (Gabelman and Hwang, 1999):

$$Sh = \frac{k_g d_e}{D_g} = 1.25 \left(\frac{d_e}{L}\right)^{0.93} \left(\frac{d_e u_g}{v_g}\right)^{0.93} \left(\frac{v_g}{D_g}\right)^{0.33} \quad \text{(B.3)}$$

where d_e is the equivalent diameter of the shell (m) and v_g the kinematic viscosity of the gas at 25^{o}C (m^2 s^{-1}).

The equivalent diameter of the shell d_e is defined as (Juang et al., 1992):

$$d_e = \frac{S_i^2 - N d_o^2}{S_i + N d_o} \quad \text{(B.4)}$$

Where S_i is the inner diameter of the shell unit (m), N the number of the fibers and d_o the outer diameter of the fiber (m)

The value of K_m which corresponds to the mass transfer coefficient within the membrane can be predicted by the following equation for both membranes:

$$k_m = \frac{D_m}{d}. \quad \text{(B.5)}$$

Where D_m is the diffusion coefficient of the compound through the membrane (m^2/s) and d is the thickness of the membrane (m) (Wickramasinghe et al., 1992).

Parameters used for the calculations of the gas mass transfer coefficients for both compounds and modules:

Compound	TCE				
L (m)	0.0391	0.0391	0.0391	0.0391	0.0391
D_g (m^2 s^{-1})	$8.34x10^{-6}$	$8.34x10^{-6}$	$8.34x10^{-6}$	$8.34x10^{-6}$	$8.34x10^{-6}$
u_g (m s^{-1})	0.0713	0.1427	0.2853	0.5707	1.1413
d_i (m)	$1.67x10^{-4}$	$1.67x10^{-4}$	$1.67x10^{-4}$	$1.67x10^{-4}$	$1.67x10^{-4}$

Table B.1. Parameters for the calculation of the gas mass transfer coefficients for the PDMS module for TCE

Compound	PCE				
L (m)	0.0391	0.0391	0.0391	0.0391	0.0391
D_g (m^2 s^{-1})	$7.61x10^{-6}$	$7.61x10^{-6}$	$7.61x10^{-6}$	$7.61x10^{-6}$	$7.61x10^{-6}$
u_g (m s^{-1})	0.0713	0.1427	0.2853	0.5707	1.1413
d_i (m)	$1.67x10^{-4}$	$1.67x10^{-4}$	$1.67x10^{-4}$	$1.67x10^{-4}$	$1.67x10^{-4}$

Table B.2. Parameters for the calculation of the gas mass transfer coefficients for the PDMS module for PCE

Compound	TCE				
L (m)	0.23	0.23	0.23	0.23	0.23
D_g (m^2 s^{-1})	$8.34x10^{-6}$	$8.34x10^{-6}$	$8.34x10^{-6}$	$8.34x10^{-6}$	$8.34x10^{-6}$
u_g (m s^{-1})	$2.03x10^{-3}$	$4.06x10^{-3}$	$8.13x10^{-3}$	$1.63x10^{-2}$	$3.25x10^{-2}$
d_e (m)	$5.04x10^{-4}$	$5.04x10^{-4}$	$5.04x10^{-4}$	$5.04x10^{-4}$	$5.04x10^{-4}$
S_i (m)	0.0425	0.0425	0.0425	0.0425	0.0425
N	7400	7400	7400	7400	7400
d_o (m)	0.0003	0.0003	0.0003	0.0003	0.0003
v_g (m^2 s^{-1})	$1.57x10^{-5}$	$1.57x10^{-5}$	$1.57x10^{-5}$	$1.57x10^{-5}$	$1.57x10^{-5}$

Table B.3. Parameters for the calculation of the gas mass transfer coefficients for the PP module for TCE

Compound	PCE				
L (m)	0.23	0.23	0.23	0.23	0.23
D_g (m^2 s^{-1})	$7.61x10^{-6}$	$7.61x10^{-6}$	$7.61x10^{-6}$	$7.61x10^{-6}$	$7.61x10^{-6}$
u_g (m s^{-1})	$2.03x10^{-3}$	$4.06x10^{-3}$	$8.13x10^{-3}$	$1.63x10^{-2}$	$3.25x10^{-2}$
d_e (m)	$5.04x10^{-4}$	$5.04x10^{-4}$	$5.04x10^{-4}$	$5.04x10^{-4}$	$5.04x10^{-4}$
S_i (m)	0.0425	0.0425	0.0425	0.0425	0.0425
N	7400	7400	7400	7400	7400
d_o (m)	0.0003	0.0003	0.0003	0.0003	0.0003
v_g (m^2 s^{-1})	$1.57x10^{-5}$	$1.57x10^{-5}$	$1.57x10^{-5}$	$1.57x10^{-5}$	$1.57x10^{-5}$

Table B.4. Parameters for the calculation of the gas mass transfer coefficients for the PP module for PCE

Compound	TCE and PCE	TCE and PCE	TCE and PCE	TCE and PCE	TCE and PCE
Standard deviation R	$6.14x10^{-6}$	$6.14x10^{-6}$	$6.14x10^{-6}$	$6.14x10^{-6}$	$6.14x10^{-6}$
Mean R (m)	$8.34x10^{-5}$	$8.34x10^{-5}$	$8.34x10^{-5}$	$8.34x10^{-5}$	$8.34x10^{-5}$
ϵ_o^2	$5.43x10^{-3}$	$5.43x10^{-3}$	$5.43x10^{-3}$	$5.43x10^{-3}$	$5.43x10^{-3}$
V (m^3)	$8.55x10^{-10}$	$8.55x10^{-10}$	$8.55x10^{-10}$	$8.55x10^{-10}$	$8.55x10^{-10}$
Qg (m^3 s^{-1})	$5.00x10^{-8}$	$1.00x10^{-7}$	$2.00x10^{-7}$	$4.00x10^{-7}$	$8.00x10^{-7}$

Table B.5. Parameters for the calculation of the average gas mass transfer coefficients for the PDMS module for TCE and PCE

CHAPTER 3

PHOTOIONIZATION DETECTOR

3.1. INTRODUCTION

There are a variety of commercially available detectors for gas phase analysis (Coy et al., 2000; Murata et al., 2004; Reimann et al., 1995; Skaggs et al., 1998). Recent instruments are capable of detecting and quantifying volatile organic compounds (VOC) in a gas phase at low parts per billion concentrations (μg l^{-1}). Typically, these devices, known as portable vapour analyzers, are used for general surveying and site investigation when identification of specific compounds is unnecessary. Those kinds of instruments often include a PID as a detector. A typical PID is small, relatively economical and easy to use because of its low power consumption and there is no need for a carrier gas (Adamson et al., 2009).

The measurement principle of the PID is based on the determination of all photoionizable compounds present in a gas phase without distinguishing the individual pollutants present in the gas/vapour phase (Poirot et al., 2004). The detector responds to most vapours that have an ionization potential less than or equal to that supplied by the ionisation source, which is a Krypton lamp. Photoionization occurs when an atom or molecule absorbs a photon of sufficient energy to release an electron and form a positive ion. The sensor is housed in a probe and consists of a source that emits photons with an energy level high enough to ionize organic compounds. The ionization chamber exposed to the source contains a pair of electrodes; a bias electrode and the collector electrode. When a positive potential is applied to the bias electrode, an electro-static field is created in the chamber (Peng et al., 2010). Ions formed by the absorption of photons are driven to the collector electrode. The current

produced is then measured and the corresponding concentration displayed on a voltmeter, directly in units above background.

This study assesses the performance of the PID detector, with respect to different substances in the gas phase. A series of experiments is carried out to measure the concentration of each compound or a mixture of the compounds using a parallel gas chromatographic analysis. These tests are done for two chlorinated solvents, TCE and PCE and four aromatic hydrocarbons: benzene, toluene, ethylbenzene and xylene.

3.2. EXPERIMENTAL SECTION

3.2.1. Materials

PID gas detector

The miniaturized high senstivity photoionization detector (MiniPID 3-pin ppb, Ionscience) is used as the gas detector, its detection range is 5μg l^{-1} to 50mg l^{-1} according to the manufacturer's specifications. A 6mm glass 10.6eV lamp filled with ultra-pure krypton gas and impurity getter for long life is installed in the detector. The precision of the detector's response is ±2% (MiniPID Use Manual, Ionscience). A calibration of the detector is necessary before its use, and on a monthly basis, as suggested by the manufacturers. The calibration is conducted by passing a gas standard of 45.8μg l^{-1} *iso*-butylene (Messer, Switzerland) through the detector, typical standard for PID's calibration. The sensitivity of the detector varies according to the compound detected. A response factor relates the PID response of a particular compound's PID to the *iso*-butylene response, which is the compound for the calibration of the detector (Table 3.1). The response factors are calculated when the instrument is calibrated with the gas standard and the units of its concentrations are in ppmv. Therefore the following formula can be used to convert the concentration from ppmv to mg m^{-3}:

$$Conc.(mg/m^3) = \frac{[Conc.(ppmv) \times mol.wt.(g/mol)]}{molar\ gas\ volume(L/mol)} \quad (3.1)$$

At 25^{o}C, the molar gas volume is 24.4L mol^{-1}.

Compound	Response factor miniPID
Benzene	0.5
Toluene	0.5
Ethylbenzene	0.5
VC	2.1
cis-DCE	0.8
TCE	0.7
PCE	0.7
TVOC	1.0
Iso-butlynene	1.0

Figure 3.1 MiniPID manufacturer's response factors for VOCs

3.2.2. Chemicals

A group of five organic compounds is selected from two different groups, i.e. aromatic hydrocarbons (benzene, toluene and ethylbenzene) and chlorinated solvents (TCE, PCE). All the solvents are of analytical grade (purity ≥99.5%, Fluka, Switzerland) and are used without further purification. Gas standards are prepared at different concentrations.

3.2.3. Analytical methods

Gas chromatography

All samples are analysed by gas chromatography using a flame ionization detector (GC-FID, CP – 3800 Varian Inc., Creek Boulevard, CA, USA). The detector temperature is set to 250^{o}C. A BGB-5 column (30m x 0.25mm I.D., 0.50μm film thickness) from BGB-Analytik (Switzerland) is used for all GC separations. The column is connected to a VICI 6port 2-position electric valve (OMNILAB AG, Switzerland) equipped with a sample loop 250ul, for

direct analysis of the gas phase samples. The following temperature program is used: 40^{o}C for 0.50min, 40-175^{o}C at 15^{o}C min^{-1}, 175^{o}C for 3min and a column flow rate of 1.5ml min^{-1}. All gas samples are collected with VICI - Valco gas tight syringes (OMNILAB AG, Switzerland) and injections are performed manually.

The calibration for the gas phase analysis is achieved by external standards containing the target compounds in the gas phase. A liquid mixture of the pure phase of the two volatile chlorinated hydrocarbons is prepared in a 250ml vial with a Mininert® valve (VICI, Switzerland) and a large headspace. The proportion of compounds in the liquid phase is chosen such that equal pressures of each compound in the gas phase are obtained. The theoretical vapour concentration in the headspace is calculated with Raoult's law assuming ideal behaviour. The calibration using external standards is linear over at least three orders of magnitude. The coefficients of correlation for the calibration are usually better than 0.99 for all compounds. The uncertainty (1σ) is ±3% for TCE, ±4% for PCE, ±3% for benzene, ±3% for toluene and ±3% for ethylbenzene.

3.2.4. Experimental setup

Stability experiments

The stability of the MiniPID is tested with a gas standard of a given concentration. This gas standard containing a mixture of all the compounds with a total concentration of 500μg l^{-1} is prepared in a bottle of 1l volume from a gas standard of 200mg l^{-1} and it is connected directly to the detector. The signal of the MiniPID detector is checked every 5min for a duration of 45min. The gas is transferred to the MiniPID chamber at a rate of 12ml min^{-1} using as carrier gas helium, which has no influence on the MiniPID signal. In addition, samples are taken for a parallel analysis by GC-FID at the outlet of the PID.

Note that there is a diminution of the concentration with time caused by the limited volume of the gas bottle. The molecular mass can be expressed by the following equation:

$$\frac{dM}{dt} = V\frac{dC}{dt} = -qC \tag{3.2}$$

From which one obtains:

$$\frac{dC}{dt} = -\left(\frac{q}{V}\right)C \tag{3.3}$$

So this diminution can be described by:

$$C_o = \frac{C(t)}{e^{-\left(\frac{q}{V}\right)t}} \tag{3.4}$$

Where C_o is the concentration of the gas standard, q the flow rate, V the volume of the bottle and t the time. Consequently, the PID's response should be corrected by dividing the every 5min response with the factor $e^{-(q/V)t}$ in order to eliminate the drift over time.

Linearity experiments for mixture and individual compounds

The linearity of the MiniPID's signal is tested for different concentrations for each compound individually. Six different concentrations are prepared 10µg l^{-1}, 25µg l^{-1}, 50µg l^{-1}, 100µg l^{-1}, 250µg l^{-1} and 500µg l^{-1} for each compound in a 2l bottle, and the signal is recorded after 10min, while each sample is analysed by GC-FID. The flow rate of the carrier gas to the PID is set to 12ml min^{-1}. Standards are prepared from the pure phases. The gas concentration C_g can be calculated by the following equation:

$$C_g = \frac{n_g}{V_g} = \frac{p_i^*}{RT} \tag{3.5}$$

With R the ideal gas constant (l bar mol^{-1} K^{-1}) and T the temperature in ^oK. The concentration in the gas phase is calculated with the vapour pressure p^*_i of each compound assuming it behaves like an ideal gas.

Flow rate experiments

The effect of the helium flow rate on the MiniPID's signal is tested for benzene, TCE and PCE. A gas standard containing 50μg l^{-1} of mixture is prepared in a 2l bottle and the signal of the detector is recorded at five different flow rates (3, 6, 12, 24 and 48ml min^{-1}) after 10min, while GC-FID analysis is conducted.

Humidity effect experiments

Additionally, the influence of humidity on the MiniPID's signal is tested, by preparing a gas standard of PCE with a concentration of 500μg l^{-1} in a 5l bottle. The PID response is checked after 10min. Then 5ml of water are added to the bottle and the signal is recorded every minute for 50min. The flow rate is set to 24ml min^{-1}. A gas chromatography analysis is made for each time the signal is recorded every minute.

3.3. RESULTS AND DISCUSSION

3.3.1. Stability experiment

Figure 3.1 shows the stability experiments of the MiniPID with a gas mixture concentration of two chlorinated hydrocarbons, TCE and PCE and three aromatic hydrocarbons, benzene, toluene and ethylbenzene. The MiniPID responds immediately, after 3s, as the gas standard starts flowing through the cell of the detector. Clearly, the detector's signal decreases over time.

Figure 3.1 depicts an exponential diminution of the signal, which follows equation 3.4, together with the corrected response over time. As shown, the PID's signal shows no drift over a period of 45min. Furthermore, if the detector is switched off for some seconds while the gas flow rate is maintained, and switched on again, the signal doesn't change as there are still VOC molecules collected in the PID chamber. If the detector is turned off for more than 3min, then the signal level returns to or close to the background value since the VOC

molecules pumped through the PID chamber are not any more in the excited state. Thus, it takes 3s to get a signal that corresponds to the concentration analyzed; consequently this is the warming time of the detector.

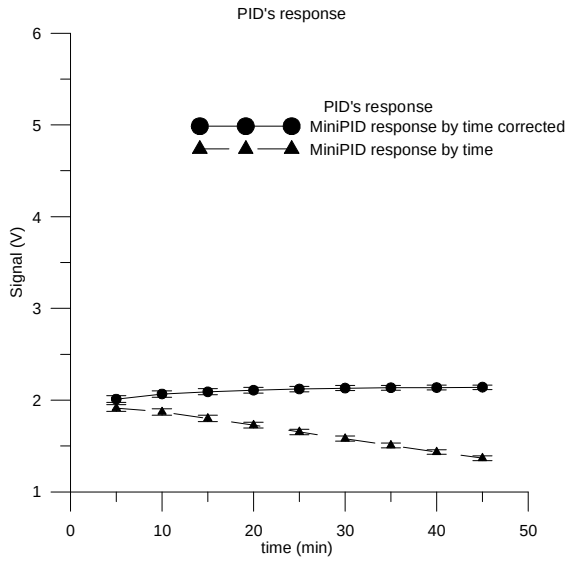

Figure 3.1 PID's response over time

3.3.2. MiniPID's linearity

Figure 3.2 presents the PID response for increasing concentrations of individual components at a flow rate of 12ml min^{-1}. All the components except benzene show a linear relation over concentrations ranging from 10 to 500μg l^{-1}. For benzene, the 250 and 500μg l^{-1}samples exhibit a response of 3.08V, corresponding to the saturation of the detector. According to the manufacturer, the response factor for benzene as presented in Table 3.1, toluene and ethylbenzene is 0.5 and for TCE and PCE the response factor is 0.7. Table 3.2 shows the theoretical (manufacturer's response) and experimental response factors of the detector for the different compounds, when the response factor relates the PID response to each compound according to the TCE response. Manufacturer's response factor is relative to *iso*-butylene. Here, this theoretical response factor is transformed to a value relative to TCE The concentration used to calculate the experimental response factor is converted to ppmv using Equation 3.1 in order to have comparable results with the manufacturer's response factors.

The experimental response factors are calculated from the average of the response factors for each concentration expressed in ppmv. The response factor for each concentration (ppmv) is calculated by dividing the signal (V) of each compound to the TCE signal (V) at the same concentration (ppmv). As it can be stated in Table 3.2, the experimental response factor for all compounds (PCE, benzene, toluene, ethylbenzene) is higher than the theoretical one comparing for the same compound.

Compound	Theoretical response factor	Experimental response factor
TCE	1.0	1.0
PCE	1.0	1.28
Benzene	0.7	0.96
Toluene	0.7	1.05
Ethylbenzene	0.7	1.18

Table 3.2 Experimental and theoretical response factors for different compounds. The PID response is related to the response of each compound relative to the response of TCE

Figure 3.2 represents the concentration response in $\mu g\ l^{-1}$. Three main observations can be made: (1) benzene shows the strongest response, (2) TCE, toluene and ethylbenzene demonstrate the same response, and (3) the response of PCE is half of the three previous components.

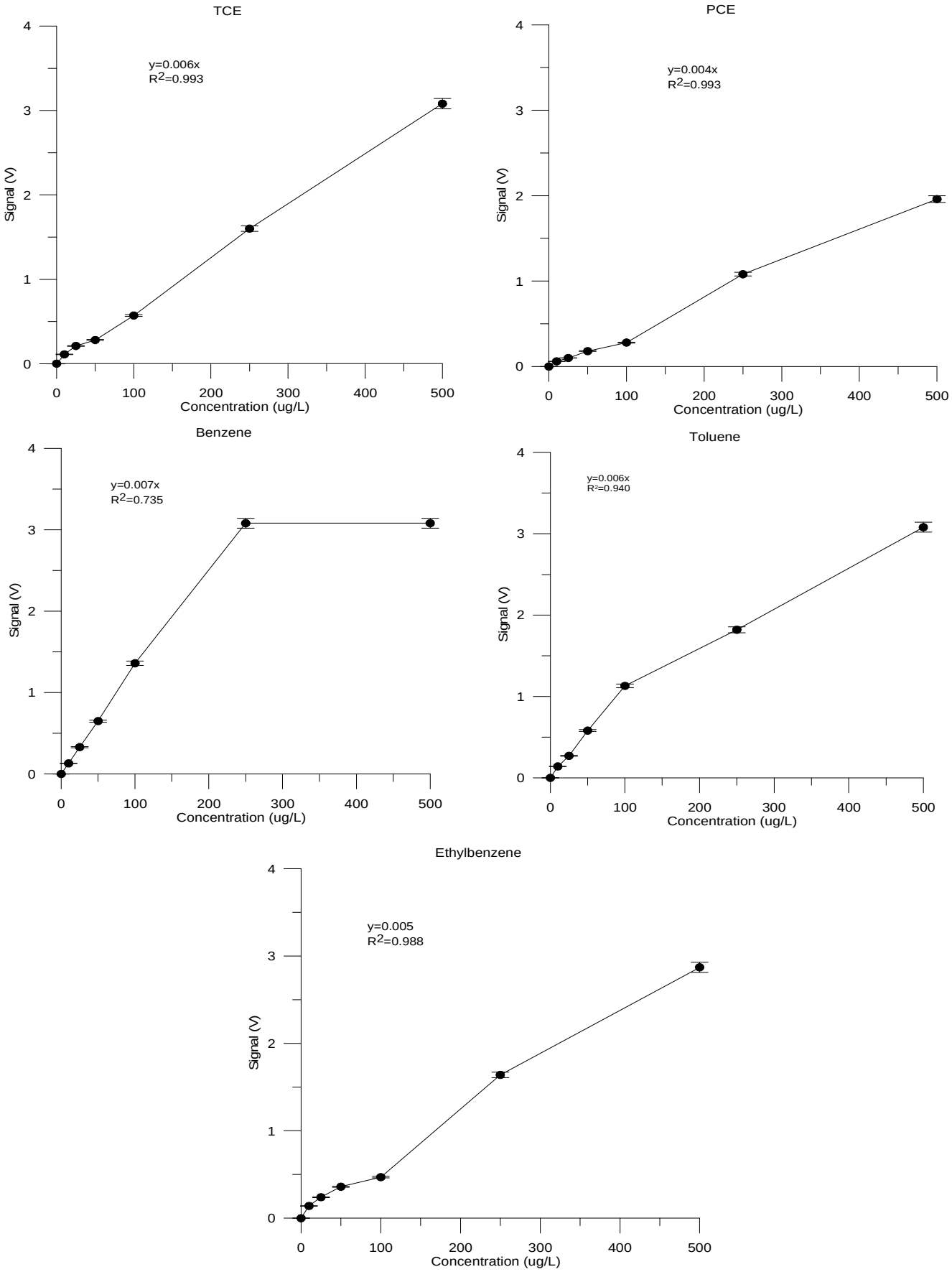

Figure 3.2 PID's signal vs. concentration for different components

3.3.3. Flow rate effect

The effect of the carrier gas flow rate on the PID signal is shown in Figure 3.3 for three of the compounds, benzene, TCE and PCE at a concentration of 50μg l^{-1} for each component. MiniPID's response appears to be independent of the gas flow rate. This result agrees with the Lambert-Beer law of light absorption (Peng et al., 2010), for which the light adsorption is proportional to the concentration absorbing species, independently of the gas flow rate. Here, the results are corrected for the drift due to the limited volume bottle.

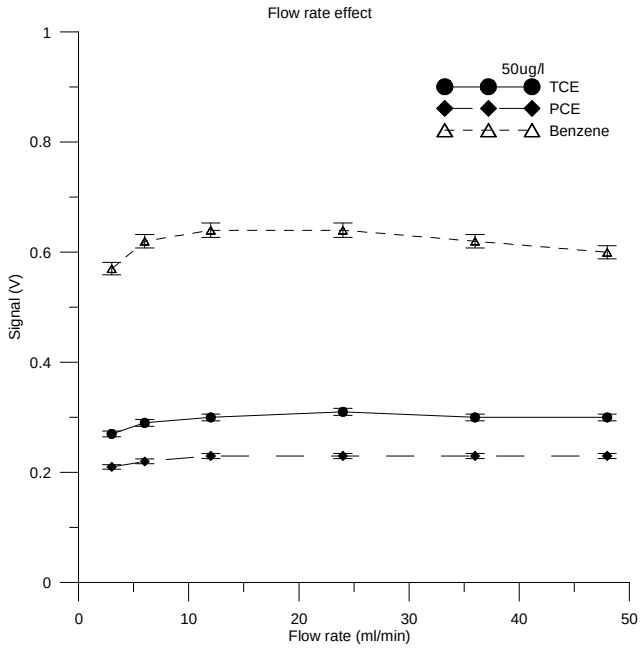

Figure 3.3 Gas flow rate effect to the PID's signal

The typical trend for the PID's flow rate mostly used for the air pollution analysis varies between 50 – 500 ml min^{-1}.

3.3.4. Humidity effect

The effect of humidity on the PID signal is shown in Figure 3.4 and the values are corrected for the drift due to the finite volume of the gas bottle used. The response of the PID in a humidified environment is about 20% lower than the response in a dry environment, thus implying that the detector is somewhat sensitive to humidity.

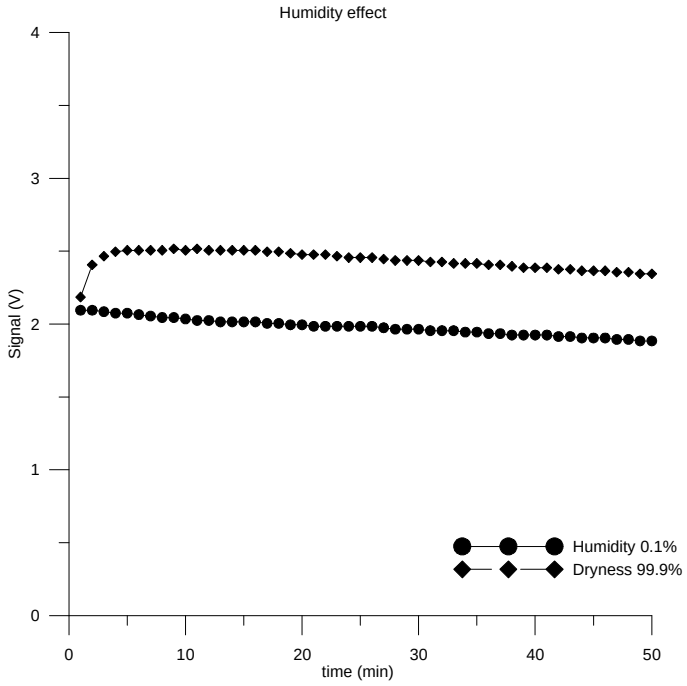

Figure 3.4 Humidity effect in PID's response

3.4. CONCLUSIONS

The MiniPID from Ionscience of high sensitivity is tested in this study for measuring chlorinated and aromatic hydrocarbons in the gas phase. The MiniPID is a small device with a large detection range from 5μg l^{-1} to 50mg l^{-1} and its response is very rapid. The detector shows highly linear response over the full tested range, 10 – 500μg l^{-1}, and a good stability over time in an experiment of 45min. However, a significant humidity effect is present which should be avoided in future experiments. Consequently, the MiniPID can be tested as a combined system with a hollow fiber membrane contactor for the sampling and analysis of chlorinated hydrocarbons in the groundwater.

CHAPTER 4

COMBINED PDMS HOLLOW FIBER MEMBRANE MODULE WITH MINIATURIZED PID GAS DETECTOR FOR FIELD ANALYSIS OF CHLORINATED SOLVENTS IN CONTAMINATED GROUNDWATER

4.1. INTRODUCTION

Since 1920, chlorinated solvents have been commonly used for various applications such as textile cleaning and in the metal processing industry. The consequence of such widespread use and often improper disposal is the existence of numerous sites contaminated with these substances. Particularly, trichloroethylene (TCE) and tetrachloroethylene (PCE), which belong to the group of dense non-aqueous phase liquids (DNAPLs), are frequently identified in contaminated groundwater and represent a substantial threat to groundwater quality because of their aqueous solubility and toxicity (U.S. Geological Survey Scientific Investigations Report, 2005). Current monitoring methods usually involve a complex procedure that requires the installation and maintenance of groundwater wells, groundwater sampling, sample transport and laboratory analysis using a sample preparation technique such as headspace, in-tube extraction or purge – and – trap combined with gas chromatography/mass spectrometry (GC/MS) (EPA SW-846, 1996). Exposure of groundwater samples to the atmosphere during these procedures can cause significant loss of volatile organic compounds (VOCs) by volatilization (Pankow et al., 1985). The laboratory methods that are used for VOC analysis are extremely versatile, sensitive and selective. However, they are expensive and do not provide real time information. On-site monitoring would benefit from a low cost alternative for the detection of chlorinated solvents in the field.

Furthermore, data can be obtained at a higher spatial and temporal resolution, thus providing additional insights in processes of contaminant release, into the fate of the contaminants in the environment or the efficacy of engineered remediation systems.

Photoionization detection (PID) as an on-site gas analyzer has been used for detecting hazardous compounds in the air. While these detectors are well suited for gas phase analysis and possess low detection limits, they are not directly applicable for groundwater monitoring.

A way to overcome these difficulties is to transfer first the compound from the aqueous phase into a gaseous phase through a membrane, and then apply the photoionization detection. The applicability of a hollow fiber membrane module as a tool for extraction of VOCs was reported in Chapter 2. In general, dense hydrophobic membranes, such as poly(dimethylsiloxane) (PDMS), have also been used for continuous extraction of VOCs followed by chromatographic monitoring and in a pervaporation technology for organic solvent recovery in other studies (Dotremont et al., 1997; Dutta and Sikdar, 1999). The pervaporation method is a membrane based process where components permeate the membrane followed by evaporation to the vapour phase, driven by the partial pressure difference of the components on either side of the membrane. In fact, membrane inlets coupled to mass spectrometry detectors have already been used to extract organic compounds from water (Camilli and Hemond, 2004; LaPack et al., 1990; Short et al., 2006).

The aims of the present work are: (1) to develop a system for on-line extraction of VOCs coupled to PID detection for on-line measurement of VOC concentrations directly in the field; and (2) to evaluate the validity of this new technique by comparing this system with a conventional method. The detection limit of the whole instrument should be below the Swiss legal limits according to OSites, at least for TCE (70µg l^{-1}) and PCE (40µg l^{-1}) which are commonly present at contaminated sites.

In this study, a PDMS hollow fiber membrane module is used for transferring dissolved chlorinated solvents into a gas stream that can be analyzed subsequently by the PID detector. The hollow fiber membrane is used with one side in contact with the aqueous sample and the other side interfacing with an air flow. The air flow is required to extract the analytes from the membrane surface and to deliver the compounds to the PID chamber. This portable dissolved VOC detector operates at low flow rate to maximize gas phase concentrations and at near atmospheric pressure. Three chlorinated solvents, TCE, PCE and *cis*-dichloroethylene (*cis*-DCE) are selected for the characterization and evaluation of this new system in the laboratory and in the field as well. Laboratory investigations were done and presented in Chapter 2, in which the use of a PDMS membrane module as an extraction tool of VOCs from water is demonstrated, and in Chapter 3, in which the performance of the PID as the detector is presented.

4.2. EXPERIMENTAL SECTION

4.2.1. Materials

Hollow fiber membrane module

The miniaturized polydimethylsiloxane hollow fiber membrane module PermSelect^{R} PDMSXA-10 (MedArray Inc., USA) is used. The module has 32 fibers knitted into an array placed inside a housing with a total active surface of 0.001m^2. During operation, the contaminated water enters the module at one side and flows over the shell side (outside the fibers) to the outlet on the other side. A stripping gas is applied to the lumen side of the module (inside the hollow fibers) countercurrently. Details about the sorption capacity of the membrane for TCE and PCE, and the extraction of these two compounds in an open system are presented in chapter 2.

PID gas detector

The miniaturized high sensitivity photoionization detector (MiniPID 3-pin ppb, Ionscience) is used as the gas detector with a detection range of 5μg l^{-1} to 50mg l^{-1}. A 6mm glass 10.6eV lamp filled with ultra-pure krypton gas and impurity getter for long life is installed to the detector. The accuracy of the detector's response is ±2%. A calibration of the detector is necessary before connecting it to the whole system. Calibration is conducted using a reference gas containing 45.8μg l^{-1} of *iso*-butylene (Messer, Switzerland) that flows through the detector. A monthly calibration is suggested according to the manufacturer. In chapter 3, details can be found for the performance of the detector regarding the stability, the range of linearity, the effect of the gas flow rate to the signal and the humidity effect on the detector.

Chemicals

For the laboratory validation, the trichloroethylene, tetrachloroethylene and *cis*-dichloroethylene solvents used in this study are purchased from Fluka (Switzerland). They are analytical grade (purity ≥99.5%) and used diluted in different aqueous concentrations.

For the chromatographic analysis of the groundwater samples, the 503.1 volatiles mix (Supelco, Switzerland), which contains TCE, PCE vinyl chloride (VC) and *cis*-DCE are used. Their concentration is 2000μg ml^{-1} in methanol and used diluted in different aqueous concentrations. Water is obtained from a Direct-Q water-purification system (Millipore S.A.S., France).

4.2.2. Experimental setup

Description and system operation

The portable dissolved VOC detector consists of the PDMS hollow fiber membrane module coupled with the MiniPID detector. A schematic diagram of the complete system is presented

in Fig.4.1. Water is pumped at a flow rate of 50ml min^{-1} through the fibers using a 12V diaphragm pump (Schwarzer Precision, SP27 RO-L, precision ±1.5%) and water is filtered before it enters the module by using a borosilicate glass filter (Whatman, GF/A 47mm), which is inserted in a stainless steel filter holder (PALL Corporation), in order to avoid clogging of the hollow fibers. A borosilicate glass filter is selected because of its non - sorptive characteristic with respect to VOCs. While the water is pumped, the volatile chlorinated solvents volatilize and diffuse through the membrane, due to the concentration gradient (Hylton and Mitra, 2007). The compounds are pulled out of the membrane by a stripping gas process using a 5V diaphragm gas pump (Micro Diaphragm pump, MDP 1304, thinXXS Microtechnology AG, precision ±1.5%) with an air flow rate of 6ml min^{-1}. The gas phase containing the compounds passes through anhydrous Na_2SO_4 to eliminate humidity and through Fe powder before entering to the detector to avoid any damage of the electronic units of the system. The latter is recommended on sites where H_2S is present. The compounds are then redirected towards the MiniPID detector, which records the voltage signal through a voltmeter.

The system is inserted inside a polyvinyl chloride (PVC) case, which is insulated with polystyrene to keep the temperature above ambient temperature and avoid condensation within the detector. It also contains a pack of silica gel to limit the humidity within the PVC case.

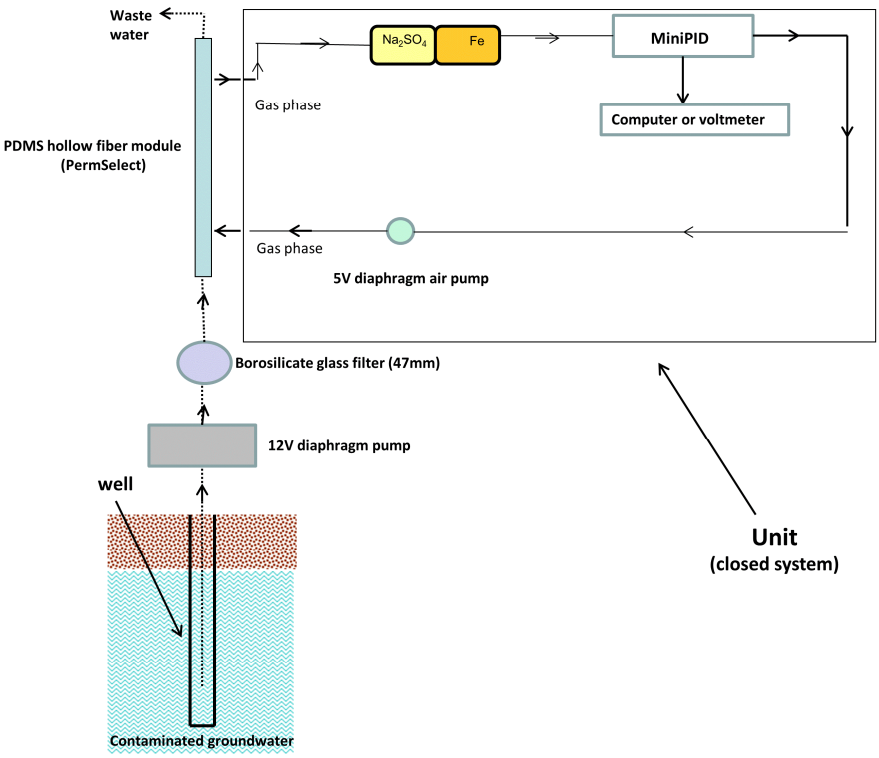

Figure 4.1 Portable dissolved VOC detector's diagram

Laboratory evaluation of the system experiments

Extraction, linearity, sensitivity and stability experiments

The portable dissolved VOC detector is tested in the laboratory by pumping through the system either a fresh aqueous solution of TCE, PCE, *cis*-DCE, or a mixture of three compounds. Individual aqueous solutions of TCE, PCE, *cis*-DCE and a mixture of them are prepared in a 10L bottle in six different concentrations: 25, 50, 100, 250, 500 and 1000μg l^{-1}. All standard solutions are prepared before each experiment from a primary standard by volumetric dilution to the required concentration levels. The mixture is prepared by adding the appropriate volume of each compound to the 10L bottle to reach the concentration given above for each compound.

In these extraction experiments, the MiniPID's signal is recorded until a steady state is reached. Furthermore, the linearity and the limit of detection of the system are investigated for

the three compounds and their mixture. Precision experiments are conducted by measuring three times each concentration by intra and inter – day measurements of each concentration over three days. The detection limit is determined by measuring a series of low concentration standards between 5μg l^{-1} and 30μg l^{-1}. The detection limit of the instrument is defined here as the signal that is at least three times the standard deviation of the blank measurement corresponding to the noise level. For this purpose, analysis of 10 standards at the estimated detection limit is done. The stability of the system is also tested by pumping an aqueous mixture standard with a concentration of 100μg l^{-1} for each compound for 1h.

Memory effect experiments

The portable dissolved VOC detector is tested for memory effects phenomena a critical factor that controls the sampling frequency of any continuous monitoring scheme. Two experiments are conducted to characterize the concentration change of the analyte that the instrument can tolerate. In the first experiment, a measurement of a 200μg l^{-1} standard mixture is followed by another one of 50μg l^{-1} until a stable reading is achieved and finally a 1000μg l^{-1} mixture solution is measured at room temperature. In the second experiment, before carrying out the concentration measurement of a new solution or sample with a known concentration, a blank solution (deionized water) is pumped through the hollow fiber membrane module on until the background of the MiniPID is reached. The signal is recorded throughout the whole experiment.

Drying tube behavior experiment

The drying capacity of the Na_2SO_4 tube was tested. For this purpose, a glass tube of a volume of 0.468ml is filled with 100mg of Na_2SO_4 and connected in series with the membrane module and the gas pump under the same conditions as all other experiments. Water is

pumped through the membrane module at 50ml min^{-1} and a humid air stream is passed through the drying tube at a gas flow rate of 6ml min^{-1}. The process is checked visually while the Na_2SO_4 absorbs water, thus controlling the pumping time and the air volume passed through the tube. As the humid air stream passes though the drying tube, which has a 1.5cm long salt bed, the front of saturated sorbent can be observed advancing down the tube. When the percentage of the liquated Na_2SO_4 reaches 50%, that means half of the drying tube is filled with water vapour and the tube can be reused, because the other half of the tube stays dry.

4.2.3. Analytical methods

Gas chromatography

All water phase samples, the initial water concentration of the laboratory experiments and the groundwater samples, are analyzed by gas chromatography equipped with a flame ionization detector (GC-FID, CP-3800 Varian Inc., Creek Boulevard, CA, USA) and an in-vial purge-and-trap (P&T) system (VSP 4000, IMT Innovative Messtechnik GmbH, Moosbach, Germany). The detector temperature is at 250^{o}C. A RT-QSPLOT column (30m x 0.32mm) from RESTEK is used for all GC separations. The oven temperature program is the following: 100^{o}C for 4min, to 240^{o}C for 5min at 10^{o}C min^{-1} and the carrier gas is He (purity 99.99%). The P&T conditions are as follow: purge 20ml min^{-1} N_2, purge time 20min, trap temp. -35^{o}C, desorb 7min at 240^{o}C, split flow 0ml min^{-1}, transfer time 140min, EPC pressure 1000mbar. The trap used is Tenax TA.

The external standard calibration is linear over at least three orders of magnitude (r^2>0.999). The uncertainty (1σ) is ±7% for VC, ±8% for *cis*-DCE, ±11% for TCE and ±8% for PCE. For all compounds, the detection limit is 0.11±0.04μg l^{-1} and the quantification limit is 0.55±0.04μg l^{-1}.

4.2.4. Field method

The VOC measurement in the field is conducted as follows: a polytetrafluoroethylene (PTFE) tube (6 x 4mm), which does not sorb VOCs (Wang et al., 2005), is inserted into the groundwater multilevel sampler to the depth of interest, and connected with the water pump (12V, Schwarzer Precision, SP27 RO-L) of the portable dissolved VOC detector. Then, the water sample is pumped to the surface and passes through the system for analysis. The compounds which are transferred to the gas phase at the exit of the hollow fiber membrane module are consequently ionized in the PID chamber and detected as an ion current.

Before starting the measurement at each location with the portable dissolved VOC detector, a parallel sampling is made by taking three samples for each location for laboratory analysis to make the comparison between the laboratory and field analysis. To obtain comparable results, a PTFE tube is put inside the piezometer at the same depth, and connected with the same water pump as described previously. Samples are taken in 40ml glass vials with an open cap and a PTFE/silicone rubber septum after pumping three times the volume of the piezometer. The samples are stored at $4^{o}C$ in an inverted position until the next day when they are analyzed. A comparison of the two techniques and thus an evaluation of the validity of the new device are presented. In order to avoid any carry over from one sampling point to another, a purging of the system is necessary. A blank solution (deionized water) is pumped through the system until the background of the PID reaches the level prior to the first measurement (baseline).

4.3. RESULTS AND DISCUSSION

4.3.1. Laboratory evaluation of the system

Extraction, linearity, sensitivity and stability experiments

Fig.4.2 shows the concentration trend for TCE, PCE, *cis*-DCE and the mixture solution as a function of time for the six different concentrations. For all concentrations tested, the steady state is reached after approximately 10 - 27min. The steady state time appears to be the same irrespective of the concentration except for PCE at higher concentrations.

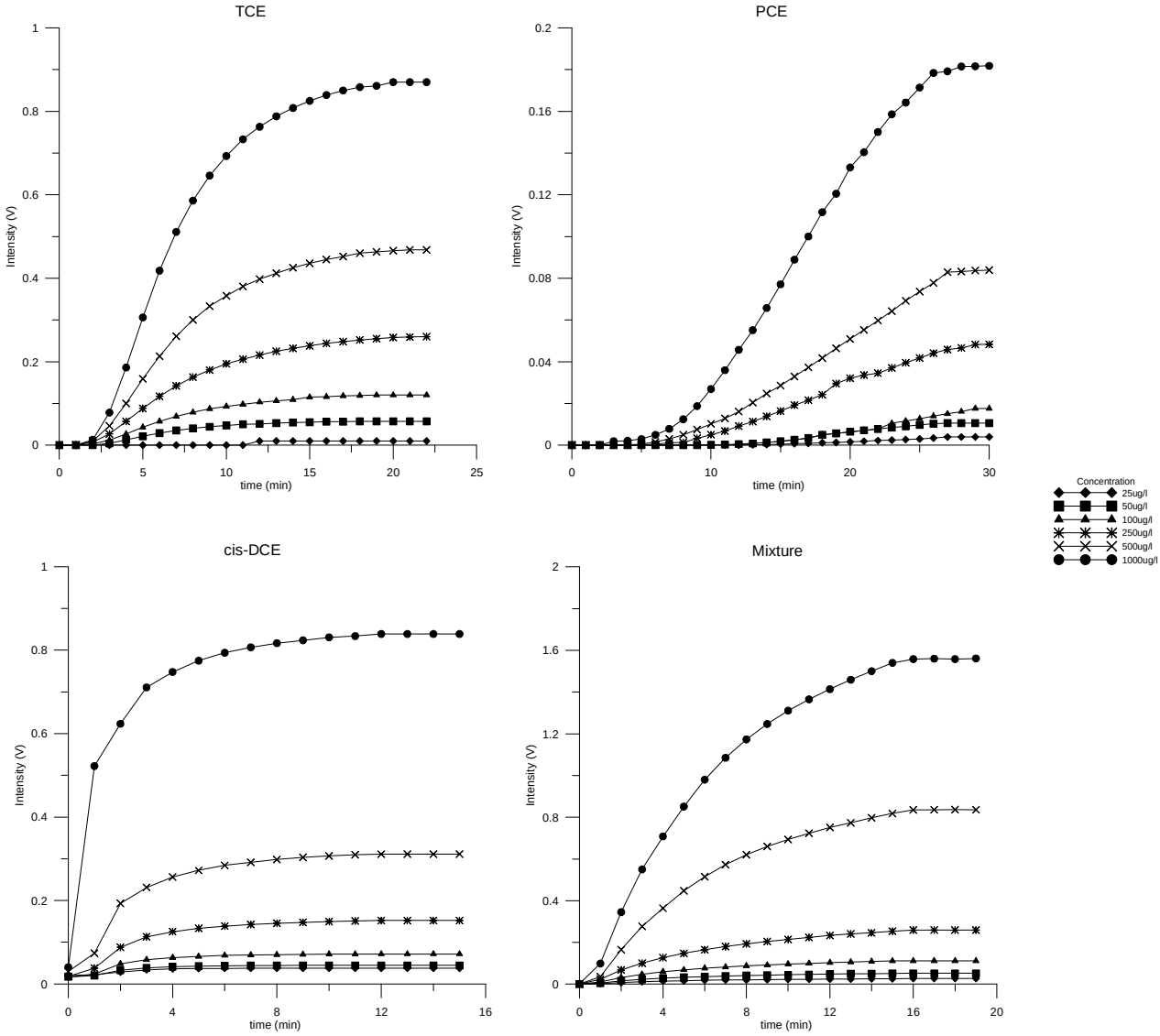

Figure 4.2 Kinetic studies for different concentrations of TCE, PCE, *cis*-DCE and a mixture of them

A comparison of the open system presented in Chapter 2 (fig.2.3) with the closed system presented in this Chapter (Fig. 4.2), shows that steady TCE and PCE concentrations are not reached at the same time. When using the open system: (a) the steady state is reached between 5 and 13 min; and (b) TCE and PCE concentrations start increasing immediately. In the closed system: (a) TCE and PCE reach steady state at 12min and 25min, respectively; and (b) TCE and PCE concentrations start increasing only after 2min and 5min, respectively. Additional time is required to achieve steady state in the closed system. As to the delay of the response time in the closed system, it probably reflects the time needed by the gas pump to build up pressure.

Figure 4.3 depicts the extraction profile curves for TCE and PCE at two different concentrations (100μg l^{-1} and 200μg l^{-1}) as a relative concentration $C_{g,\,out}/C_{q,\,eq}$. The maximum extraction of TCE is close to 50% and of PCE is close to 30%. In Chapter 2 the extraction profile curves for TCE and PCE are presented in the open system (Fig 2.3 and 2.4), the maximum extraction of TCE reaches 50% and of PCE 20%. In the close system presented here, as the gas flow rate circulates several times through the hollow fiber membrane and the detector, it would be expected that the system gets closer to the equilibrium, as molecules accumulated during recirculation until the concentration gradient is very low. In spite of this, the relative concentration for TCE reaches the same level as in the open system and the relative concentration for PCE is 10% higher than in the open system. Probably somewhere in the system there is a loss of the compounds but this loss has not been identified, but it doesn't seem to have any influence on the linearity of the system's response and on repeatability of the measurements as it can be seen below.

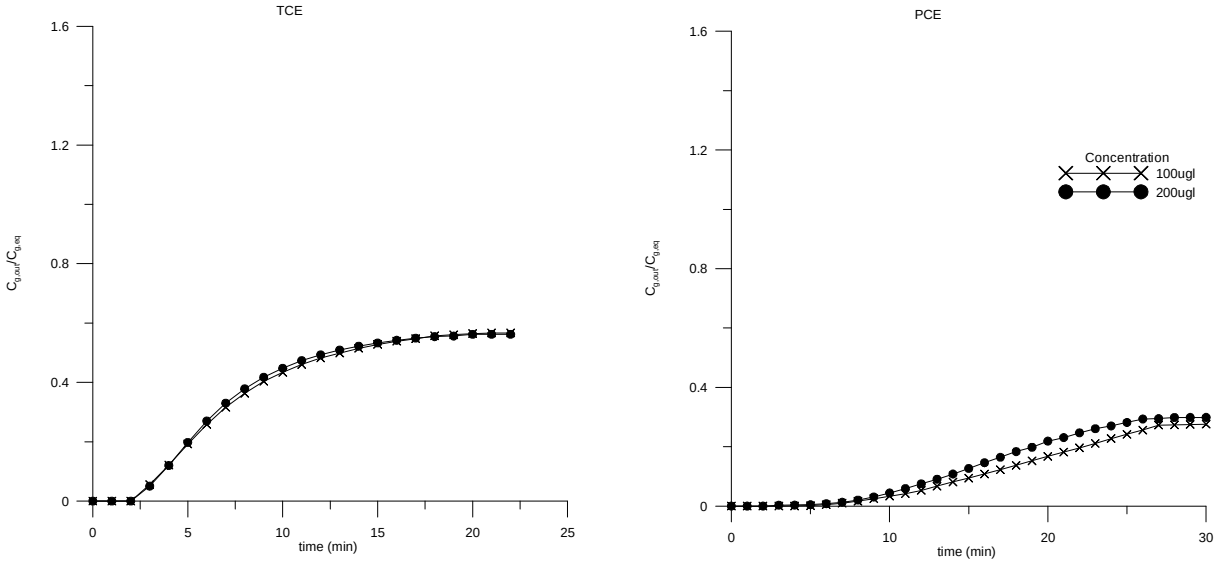

Figure 4.3 Extraction profile curves for TCE and PCE at two different concentrations

The response of the system is investigated for different concentrations of each compound separately and with a mixture of them; the results are shown in Fig.4.4. The detection limit of the portable dissolved VOC detector is determined, as described in Section 4.2.2, at 15±2.22μg l^{-1} for TCE, 25±2.87ugμg l^{-1} for PCE, 10±2.28μg l^{-1} for *cis*-DCE and 20±2.10μg l^{-1} for the mixture. *Cis*-DCE has the lowest detection limit, followed by TCE and then the mixture and PCE. Figure 4.3 shows that the relative concentration is not equal to 1 for TCE and PCE, as expected, because of this unidentified loss as mentioned previously. The detection limit is influenced by two factors: (1) the Henry's coefficient and (2) the response of the detector for each compound. The detection limit is influenced by the Henry's coefficient which determines the capacity of gas as presented in Chapter 2, so TCE with a lower *H* will have a higher relative concentration than PCE (Table 2.3). The Henry's coefficient of *cis*-DCE is almost half compared to TCE (Table 4.1), which means that its relative concentration should be higher than TCE's and PCE's. Consequently, *cis*-DCE has a lower detection limit than TCE, and TCE has a lower detection limit than PCE, which agrees with the results. In Chapter 3, the experimental response factors of the PID detector are shown for TCE and PCE. It is found that TCE has a stronger response than PCE (Fig. 3.2), consistent with its lower

detection limit. The time to reach steady state (Fig. 4.2) demonstrates a similar trend as the detection limit; *cis*-DCE reaches steady state first, and then follows TCE, the mixture and finally PCE. This trend is due to the sorption into the PDMS membrane. In Chapter 2 (Fig. 2.2), TCE appears to sorb less into the PDMS membrane than PCE which results in a longer stabilization time. The sorption is related to the compound's hydrophobicity, the more hydrophobic compound shows a stronger sorption on the hydrophobic PDMS membrane. In Table 4.1, the K_{OC} values are presented for the three compounds. In our experiments, the less hydrophobic *cis*-DCE reaches a stable concentration faster followed by the average hydrophobic TCE and finally the more hydrophobic PCE.

Compound	K_{OC} (ml g^{-1}) 25°C	H (dimensionless) 25°C	H (dimensionless) 9°C
cis-DCE	36	0.16	0.08
TCE	97	0.43	0.19
PCE	265	0.76	0.31

Table 4.1 Physicochemical parameters of *cis*-DCE, TCE and PCE (Schwarzenbach et al., 2003; US EPA, 1996; US EPA On-line Tools for Site Assessment Calculation)

Consequently, the order of the compounds starting with the compound that needs less time for steady state is *cis*-DCE > TCE > PCE.

Furthermore, the mixture solution shows an average behavior compared to the other compounds with a detection limit of 20±2.10μg l^{-1} and a response time close to 20min. Observing Table 4.2, the mixture solution of a certain concentration has a different proportion in a mol basis of each compound. *Cis*-DCE has a greater concentration in mol basis in the mixture for the same concentration expressed in weight basis, followed by TCE and then PCE. According to Fig. 4.2 the mixture solution reaches steady state at the same time as TCE, and shows an average sensitivity compare to the three other compounds. This is because of

the different proportion of molecules of each compound in the mixture and as discussed previously the maximum extraction is different for the three compounds.

Mixture	*cis*-DCE	TCE	PCE
Concentration ($\mu g\ l^{-1}$)	Concentration (umol l^{-1})	Concentration (umol l^{-1})	Concentration (umol l^{-1})
25	0.26	0.19	0.15
50	0.52	0.38	0.30
100	1.03	0.76	0.60
250	2.58	1.90	1.51
500	5.16	3.81	3.02
1000	10.31	7.61	6.03

Table 4.2 Concentration of each compound to the mixture in mol basis

As a result, not only the response, but also the slopes of the calibration curves should vary for the three compounds independently and for the mixture, as it happens in our case (Fig. 4.4) Furthermore, the signal of the portable dissolved VOC detector shows to be linearly dependent on concentration over the range tested (Fig. 4.4).

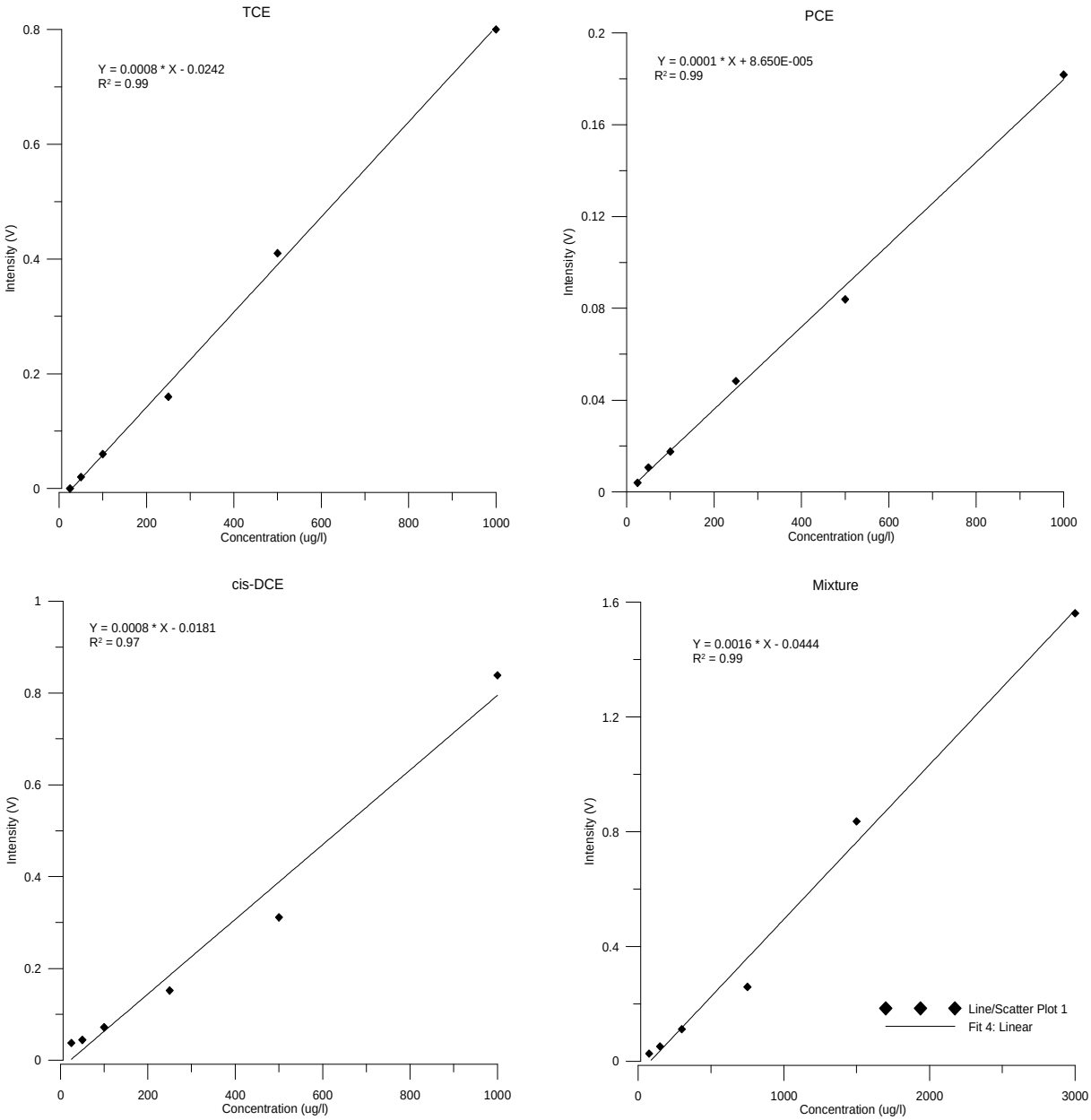

Figure 4.4 Calibration curve for TCE, PCE, *cis*-DCE and mixture. For the mixture, the total concentration is given.

The precision of the portable dissolved VOC detector, as calculated from the 10 point inter-day (in 3 days) standard deviation of the known concentration of 100µg l^{-1}, is 10% for TCE, 15% for PCE, 10% for *cis*-DCE and 10% for the mixture.

The stability of the whole system is presented in Figure 4.5. A mixture solution is pumped through the system under constant conditions for 1h. The system shows a response with a 20% signal drop after 60min. There is a difference between the stability of the whole system

presented here and the stability of the detector alone presented in Chapter 3, where the detector shows no drift. In this experiment, the solution used was prepared in a bottle with a headspace. The mixture's solution was prepared in a bottle, so when pumping water through the hollow fiber module, the headspace's volume of the bottle was increasing with time and thus the water concentration entering the module was decreasing slightly with time. This can explain the response's drop presented here.

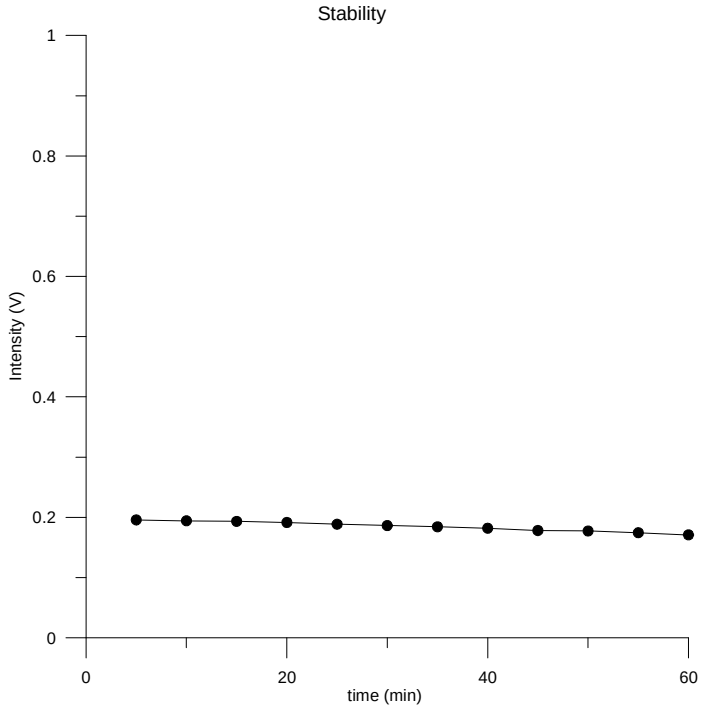

Figure 4.5 Portable dissolved VOC detector's stability over time

Memory effect experiment

Figure 4.6 shows the TCE response with an alternate pumping of a solution; firstly, a higher concentration solution is pumped followed by a lower concentration solution and then a higher concentration solution again. The response and the stabilization time of the system are significantly longer when switching the solution's concentration from a higher to a lower concentration because of a memory effect (Fig. 4.6). Based on this, it can be concluded that it

is difficult to perform on-line continuous monitoring. However when applying a blank sample (deionized water) between two measurements, the response time is improved, resulting in lower response time of 10min when switching the solution's concentration from 200μg l^{-1} to 50μg l^{-1} (Figure 4.7).

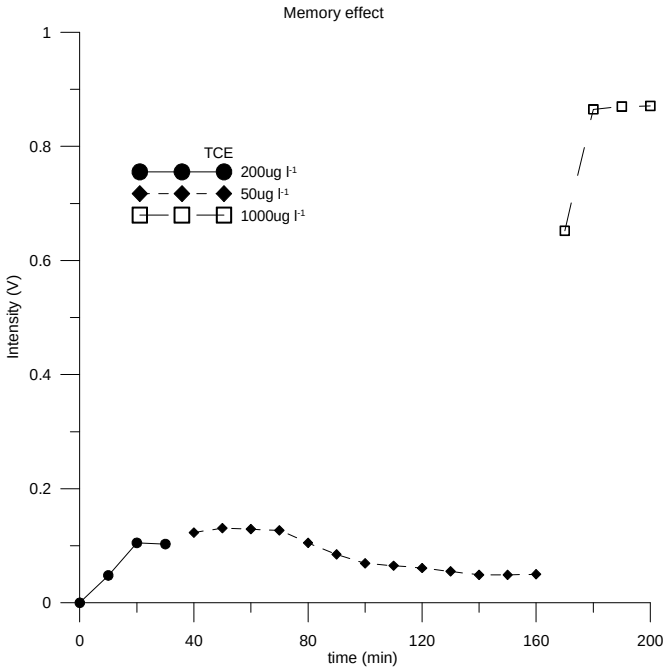

Figure 4.6 Measured continuous intensity of three different TCE concentrations for evaluation of the memory effect

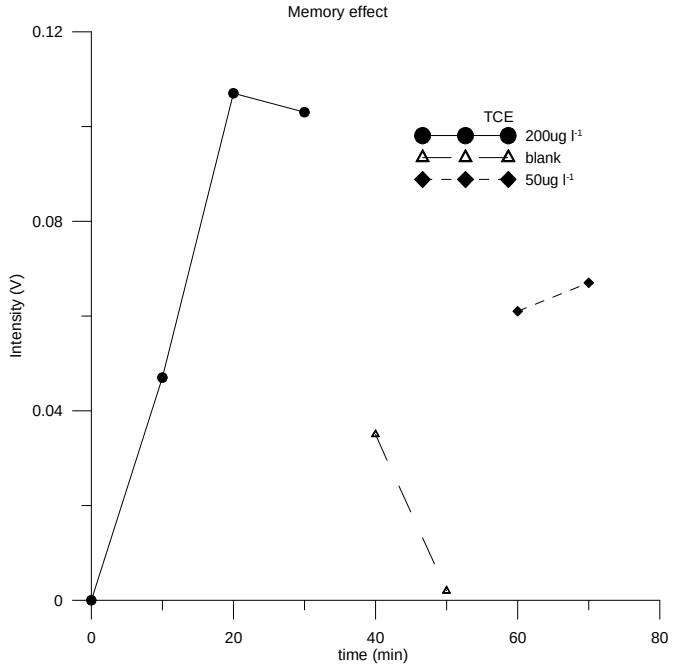

Figure 4.7 Measured continuous intensity of two different TCE concentrations with a blank applied between the measurements

Drying tube behavior experiment

Figure 4.8 shows the effect of the humid air volume on the drying tube with a volume of 0.468ml packed with Na_2SO_4. Once 2L of air are passed through the tube, 25% of the salt bed is filled with water vapor. Therefore when the air sample is limited to 2L, the drying tube can be used at least 3 times. For a better efficiency of the drying tube, it is recommended to use $CaSO_4$, as it is more stable in humidity.

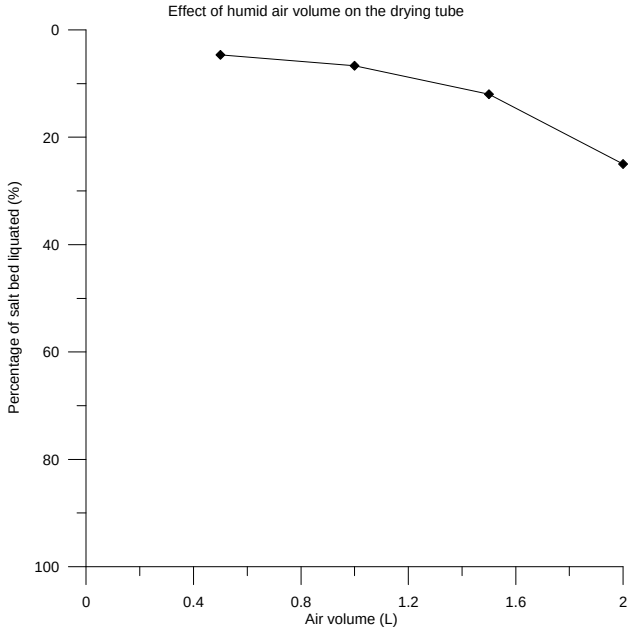

Figure 4.8 Effect of the humid air volume on the liquation of Na_2SO_4 drying tube

4.3.2. Field evaluation

To assess the portable dissolved VOC detector under field conditions, the prototype is used to monitor groundwater at a contaminated site, located in the military area in Lyss in the canton of Bern (Switzerland), where a multi – level sampling network is installed (Ducommun et al., Article in preparation). VOC concentrations are obtained through conventional groundwater sampling and P&T GC - FID analysis. Plots of the measured concentrations with the prototype calculated from the calibration curve for the mixture presented in Fig. 4.4, and measured concentrations from the data obtained of traditional analysis with P&T GC – FID are shown in Fig. 4.9 for selected sampling points measured in August 2010. The total concentration of VOCs is the sum of VC, *cis*-DCE, TCE and PCE concentrations obtained by P&T GC-FID. The total uncertainty for the total GC-FID concentration is 40%, obtained from the summation of each compound's uncertainty mentioned in this Chapter (Section 4.2.3). The total uncertainty for the prototype's measurements is 10% which is the precision of the portable dissolved VOC detector for the mixture. It is assumed that no interaction occurs

among the compounds. This method is not compatible for the analysis of the hydrophobic methane and freons, as the PID detector cannot detect these compounds.

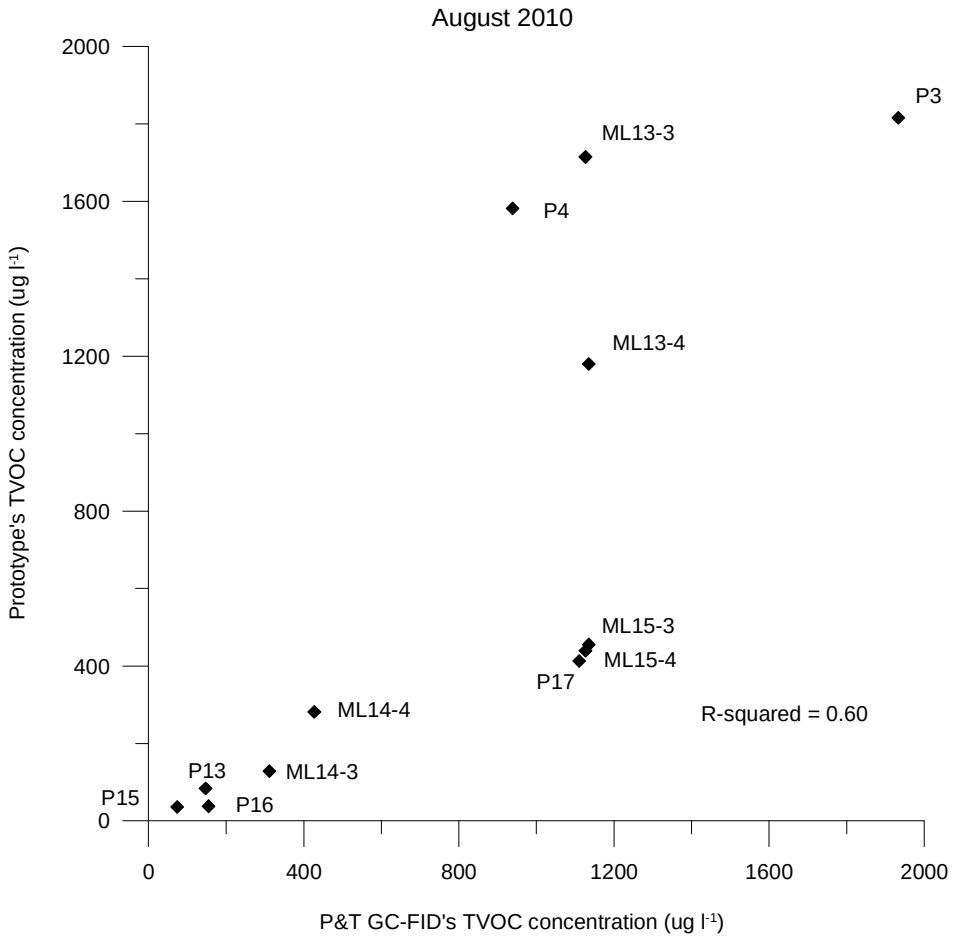

Figure 4.9 Plot of the total VOC concentration measured with the portable dissolved VOC detector and the total concentration measured by P&T GC-FID data for 11 different locations in August 2010

Observing Fig. 4.9, there is a correlation with an R^2 equal to 0.60 between the two measurements, field and laboratory. This correlation has almost a ratio 1:1, mainly for the higher concentrations. At locations ML14-3, ML14-4, ML15-3, ML15-4, P3, P13, P15, P16 and P17 the prototype shows lower concentrations than the laboratory measurements. It must be noted that in the laboratory measurements, the total concentration includes VC as this compound is present in the field, which was not included in the calibration of the portable system. Thus, the calibration curve used for the field measurements includes only the 3 other

compounds, *cis*-DCE, TCE and PCE. Furthermore, the temperature of the samples measured with the prototype in the field is lower than the temperature of the aqueous solutions used for the calculation of the calibration curve equation. A decrease of the temperature means that the Henry coefficient decreases too and thus fewer molecules are in the gas phase. The lower concentrations measured by the portable device show a difference of a factor of 2 to 3 times comparing to laboratory measurements. The water's field temperature was at 9^{o}C; at this temperature the Henry's coefficient is about 2.5 times lower than the one at 25^{o}C (Table 4.1). This can explain the lower concentrations measured by the portable dissolved VOC detector.

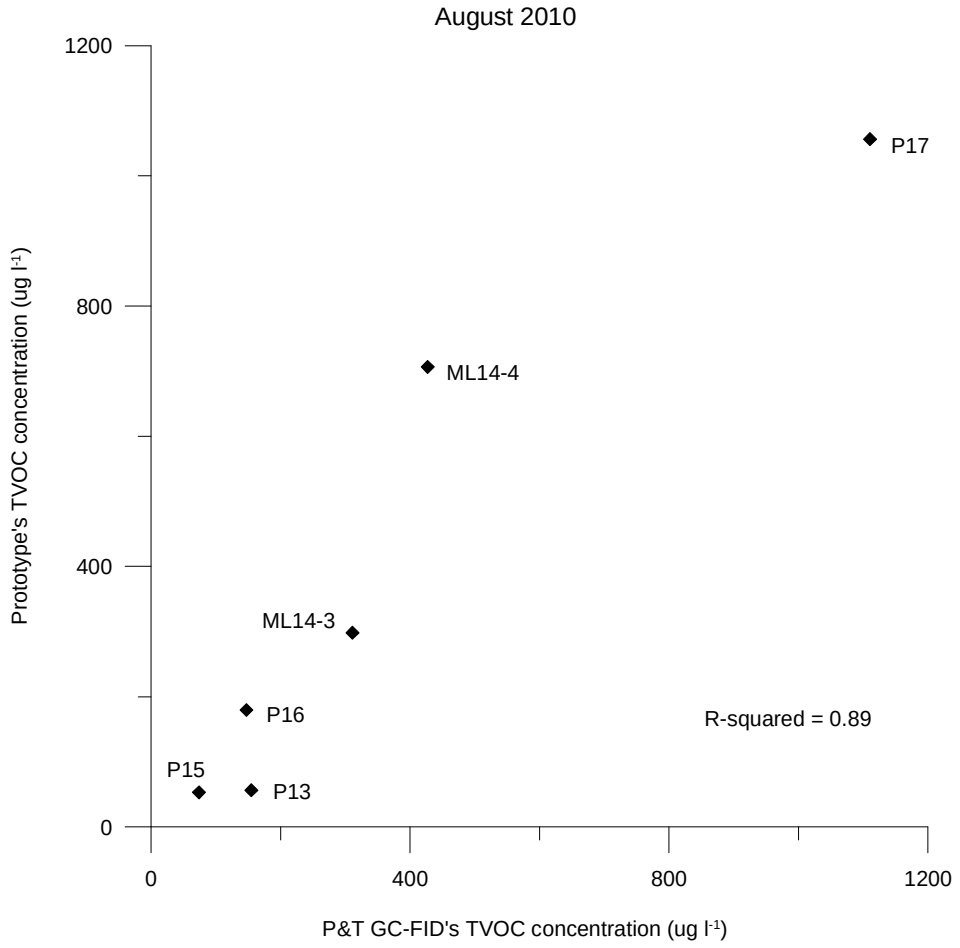

Figure 4.10 Plot of the total VOC concentration measured with the portable dissolved VOC detector and corrected for the effect of the temperature dependence of the Henry coefficient and the total concentration measured by P&T GC-FID data for 6 different locations in August 2010

By correcting the signal of the portable VOC detector for the Henry's coefficient temperature dependence as showed in Figure 4.10, the correlation between the two measurements, in field and in the laboratory, is improved (R^2 equal to 0.89) for the points where the VC is absent or its concentration is very low.

A further field investigation over time should be done at the sampling points to confirm these results during one month measurements. Also, in field conditions to avoid memory effect it is necessary to pump a blank solution (deionized water) through the system between two different sampling points, especially when high concentrations are measured (>400μg l^{-1}). It is observed that after the measurement of the sampling point with the highest concentration, the time needed for the instrument to reach again the baseline is 20min.

4.4. CONCLUSIONS

A combined PDMS hollow fiber membrane module with a miniaturized PID detector is tested as a single procedure of sampling and analysis for field measurement of chlorinated solvents in contaminated groundwater. The PDMS hollow fiber membrane is the extraction step to transfer the volatile compounds from the aqueous phase to the gas phase. The miniPID detector is subsequently connected to the membrane module, where the compounds are present in the gas phase and they can be detected. The detection limit for a mixture is 20±2.10μg l^{-1} and the stabilization time for a mixture is close to 20min. This detection limit is lower that the OSites Swiss legal limits for TCE (70μg l^{-1}) and for PCE (40μg l^{-1}). Comparing the three compounds tested, *cis*-DCE, TCE and PCE, the order with the lower detection limit and stabilization time is *cis*-DCE > TCE > PCE. The sensitivity of the system depends on the Henry's coefficient of each compound and the detector's response. The stabilization time shows to be related to the hydrophobicity of each compound. The system could be extended for the measurement of other organic compounds, like benzene, toluene, ethylbenzene, xylene

or other hydrocarbons, having in mind their physicochemical parameters and response factors of the detector. For example, it is expected that benzene should have a lower detection limit than the compounds tested here, as in Chapter 3, it showed the strongest PID's response and it has a lower *H* (Schwarzenbach et al., 2003). Moreover, its stabilization time should be longer than *cis*-DCE's and shorter than TCE's, as benzene's hydrophobicity is in the middle between these two compounds (US EPA, 1996). Certainly a calibration with known concentrations of the compounds is necessary for the concentration measurement. The overall precision of the instrument is determined at 10% calculated when using a mixture solution. On-line continuous monitoring is limited by memory effects of the hollow fiber however the portable dissolved VOC detector offers potentially large advances in site characterization; it could be a useful tool for the location of the contamination source and the following up after site remediation. Parallel sample collection for laboratory validation indicates a comparable estimation of subsurface contamination. Hence, the portable dissolved VOC detector demonstrates the benefit of in field measuring of chlorinated hydrocarbons in groundwater, so additional studies in the field during a longer period is intended so test the stability of the instrument over time.

CHAPTER 5

FIELD APPLICATION OF A PORTABLE DISSOLVED VOC DETECTOR FOR MONITORING CHLORINATED SOLVENTS IN GROUNDWATER

5.1. INTRODUCTION

High quantities of volatile organic compounds (VOCs), as trichloroethylene (TCE) and tetrachloroethylene (PCE), are also referred to as dense non-aqueous phase liquids (DNAPLs), have been used in a wide variety of industries. Widespread use and poor handling have resulted in environmental contamination, including water contamination (Fawell and Gowers). As these compounds are very volatile they are usually not present in high concentrations in surface waters. However, as dense solvents with low viscosity, they rapidly migrate downwards after a spill in groundwater (Fawell and Gowers). Surveys have frequently found aquifers in urban and industrialized areas to be contaminated by chlorinated solvents, sometimes above regulatory limits (Fawell and Gowers).

The determination of chlorinated solvents in groundwater is an important analytical problem. The commonly accepted method for analysis of volatile organic priority pollutants involves obtaining water samples from the field, transporting them to the laboratory, and analyzing them by a specific procedure. Water often contains more than one single pollutant, and the most frequently applied methods for analysis include an extraction step combined with gas chromatography (EPA SW-846, 1996). These methods are time-consuming, labor-intensive, expensive, and they do not provide on-site measurements. The on-site investigation of VOC concentrations would be a low cost alternative to traditional techniques and can enable a larger number of sampling points. Furthermore, data can be obtained in higher spatial and temporal resolution for the same cost, which can provide useful information about the release of the

contaminants, the fate of the contaminants in the environment and the performance of remediation methods.

In the previous chapter, a portable system using a polydimethylsiloxane (PDMS) membrane module coupled with a photoionization detector (PID) is presented for field analysis of chlorinated solvents in groundwater. The system provides semi-continuous measurements of total VOC concentrations in an aqueous environment contaminated with known compounds. The system operation involves the transport of the dissolved chlorinated solvents into a stream of air through a PDMS hollow fiber membrane module followed by analysis by a PID connected to the membrane module at a low air flow rate.

The present work reports the application of this measurement for monitoring chlorinated solvents in groundwater. A five month field evaluation is made to test the portable dissolved VOC detector at the same sampling points over a longer period to observe the stability of the system. The response of the instrument is compared to concentration obtained by a gas chromatography (GC) laboratory measurement.

5.2. EXPERIMENTAL

5.2.1. Site description

The military site of Lyss situated in the Seeland region, Switzerland, was contaminated by chlorinated solvents, mainly PCE during the exploitation of a dry cleaner station. This site is equipped with multi-level sampling systems, which allow for sampling at discrete depths. Further details of the hydrogeology, the multi-level systems and the characterization of the site are given in Ducommun et al. (article in preparation). Figure 5.1 shows the sampling points close to the source. Eight points are selected, P1-P4 and ML13-1 – ML13-4 for monitoring the total concentration once per month during a five-month period.

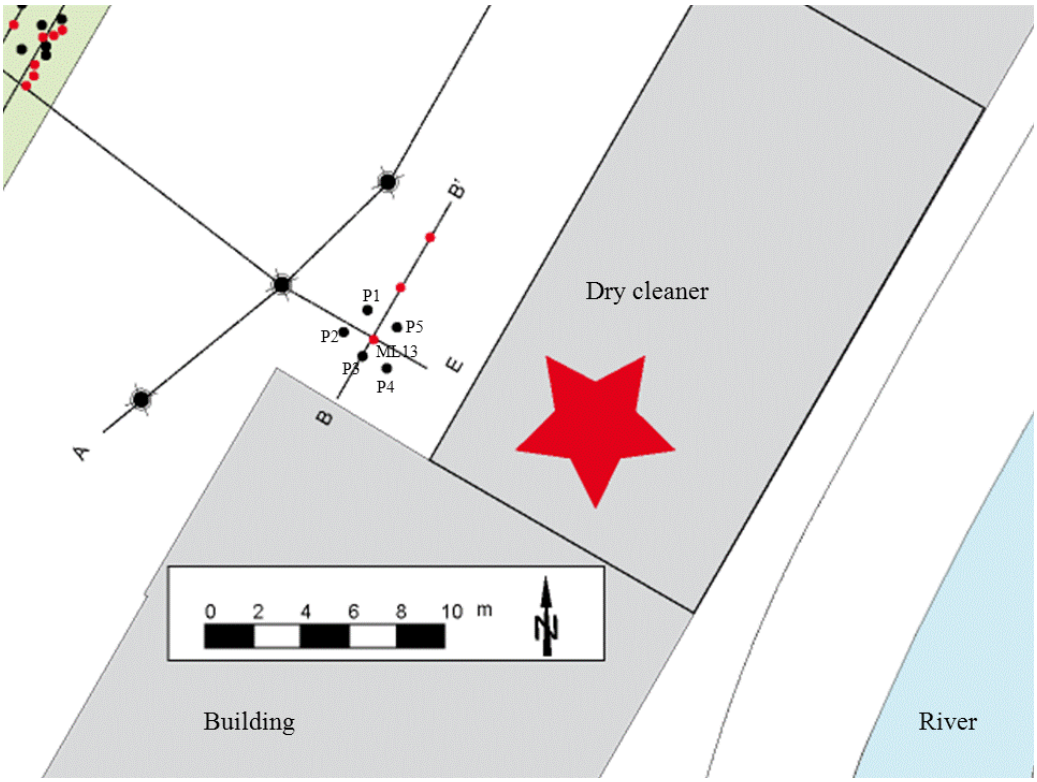

Figure 5.1 Location plan of the sampling points in the military area of Lyss, Switzerland

5.2.2. Sampling and analysis of chlorinated solvents from groundwater

The portable dissolved VOC detector is deployed for the measurement of dissolved chlorinated solvents in the groundwater (Fig. 5.2). The measurement set up for field investigation consists of a water pump, a polydimethylsiloxane (PDMS) hollow fiber membrane module for the extraction of VOCs in the gas phase, the PID detector, a gas pump and a voltmeter as described in Chapter 4. The PID detector is calibrated with a gas standard of 45.8µg l^{-1} of *iso*-butylene (Messer, Switzerland) to ensure data quality before each sampling campaign. The VOC measurement in the aqueous phase is conducted as described in Chapter 4..

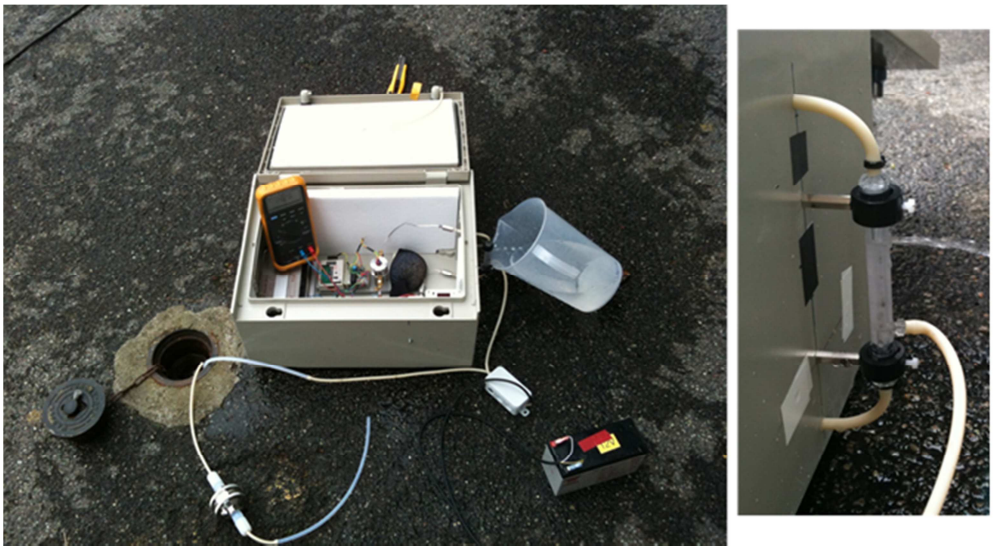

Figure 5.2 Portable dissolved VOC detector

The water pumping rate is set to 100ml min^{-1} for 15 – 20min until the PID signal stabilizes and the gas flow rate is set at 6ml min^{-1}. The detector is connected to a data logger, which records voltage. In order to avoid any carry over from one sampling point to another, a purging of the system is necessary. A blank solution (deionized water) is pumped through the system until the background of the PID reaches the level prior to the first measurement (baseline). Thus, an intensity in volt is obtained for each sampling point repeating this procedure. The calculation of the concentration for each point is made by using the equation of the calibration curve for the mixture presented in the previous chapter (Fig. 4.4). The uncertainty of the whole system is 10% as calculated for a mixture solution of *cis*-DCE, TCE and PCE (see previous Chapter).

Before starting the measurement at each location with the portable dissolved VOC detector, a parallel sampling is made by taking three samples for each location for laboratory as described in Chapter 4. Laboratory analysis is performed by gas chromatography equipped with a flame ionization detection (GC-FID, CP-3800 Varian Inc., Creek Boulevard, CA, USA) and an in – vial purge – and- trap (P&T) (VSP 4000, IMT Innovative Messtechnik GmbH, Moosbach, Germany). A RT-QS PLOT column (30m x 0.32mm, RESTEK) is used for the GC separation. The temperature program starts at 100^{o}C for 4min and then to 240^{o}C for 5min at a rate of 10^{o}C

min^{-1}. The detector is set at 250°C and the carrier gas is helium (He, purity 99.99%). The P&T conditions are the following: purge N_2 20ml min^{-1}, purge time 20min, trap temperature -35°C, desorption at 240°C for 7min, split flow 0ml min^{-1}, transfer time 140min and EPC pressure at 1000mbar. The type of trap is Tenax TA.

Linear calibration curves are based on external standards (r^2>0.999). The uncertainty (1σ) for vinyl chloride (VC) is ±7%, for *cis*-dichloroethylene (*cis*-DCE) is ±8%, for trichloroethylene (TCE) ±11% and for tetrachloroethylene (PCE) is ±8%. For all compounds, the detection limit is 0.11μg l^{-1} and the quantification limit is 0.55μg l^{-1}.

5.3. RESULTS AND DISCUSSION

5.3.1. Comparison of the portable dissolved VOC detector to conventional analysis

Plots of the total VOC concentration measured with the portable dissolved VOC detector and the total VOC concentration measured by using P&T GC-FID data for five sampling campaigns are shown in Figure 5.3. Four chlorinated hydrocarbons are detected in the groundwater, VC, *cis*-DCE, TCE and PCE. Fig. 5.3 shows the correlation between *in situ* and laboratory concentrations. The equation used for *in situ* measurements does not include the presence of VC. Results of both procedures show generally a correlation for the points measured over the 5-month period, with a correlation coefficient R^2 ranging from 0.63 to 0.75.

In most points, the laboratory measurements give higher concentrations and this underestimation of the prototype is due to the lower temperature during field analysis than the solutions temperature used for the laboratory experiments. As explained in Chapter 4, the Henry's coefficient is lower at a lower temperature and so fewer molecules are transferred to the gas phase. The concentrations measured by the portable device show a difference of a factor of 1.5 to 3.5 times compared to laboratory measurements. The water's field temperature was at 9°C; at this temperature the Henry's coefficient is about 2.5 times lower than the one at 25°C.

Consequently, a lower concentration expected to be measured in the field with the portable prototype. Furthermore, as mentioned before, the equation used to calculate the field concentrations does not include VC, a compound present in the groundwater.

When considering every month separately, in November 2010, the correlation coefficient R^2 is equal to 0.63. Locations P1, ML13-1, show a good match. In contrary P2, P3, P4 and ML13-2, ML13-3, ML13-4 have a larger *in situ* concentration.. In December 2010, a correlation coefficient R^2 equal to 0.72 is obtained. Fig. 5 shows that most of the points (P2, P3, P4, ML13-2, ML13-3 and ML13-4) have a higher laboratory concentration relative to *in situ* measurements. In January 2011, a correlation coefficient R^2 of 0.69 is observed. Whereas four points (P2, P3, ML13-2, ML13-4) have a greater laboratory concentration, one point (P4) has a larger field concentration. In February 2011 and March 2011, the correlation coefficients R^2 are 0.75 and 0.71, respectively. Three of the points demonstrate greater laboratory concentrations (P4, ML13-2, ML13-3 in February and P2, ML13-2 and ML13-3 in March). Location ML13-4 for both months shows a greater prototype concentration. According to Table 5.2 the compound composition at each point, when the VC's concentration is the lowest comparing to the three others (*cis*-DCE, TCE, PCE) or at the same level, prototype's concentrations are lower than those measured in the laboratory. When another compound has the lowest concentration and not VC, prototypes' concentrations are greater. The portable instrument measures VC and so the system's response might be higher than for the other compounds. So, the VC's concentration, which is not included in the equation used to calculate the field concentrations, increases the prototype's response when the other three compounds, *cis*-DCE, TCE or PCE have a a lower concentration. Finally, when concentrations measured are close to the detection limit of the portable device, there is a very good correlation between the two methods.

It should be noted that the detector is calibrated for each sampling day to compensate for variations in response between different days. P2 in January and March 2011 and ML13-2 in

November and December 2010 are the two points which have almost the same concentrations for each compound (Table 5.2). The system's signal for these points in two different months gives a similar voltage as it is shown in Table 5.1, so the measurement system is stable for different sampling days.

Correcting the signal of the portable VOC detector for the Henry's coefficient temperature dependence as showed in Figure 5.4, the correlation between the two measurements, in field and in the laboratory for the points where the VC is absent or its concentration is very low, is improved with correlation coefficients (R^2) equal to 0.85 to 0.99.

Sampling point	**Voltage (V)**
P2 January 2011	0.039
P2 March 2011	0.026
ML13-2 November 2010	0.010
ML13-2 December 2010	0.010

Table 5.1. System's signal for sampling points with almost the same concentrations for each compound

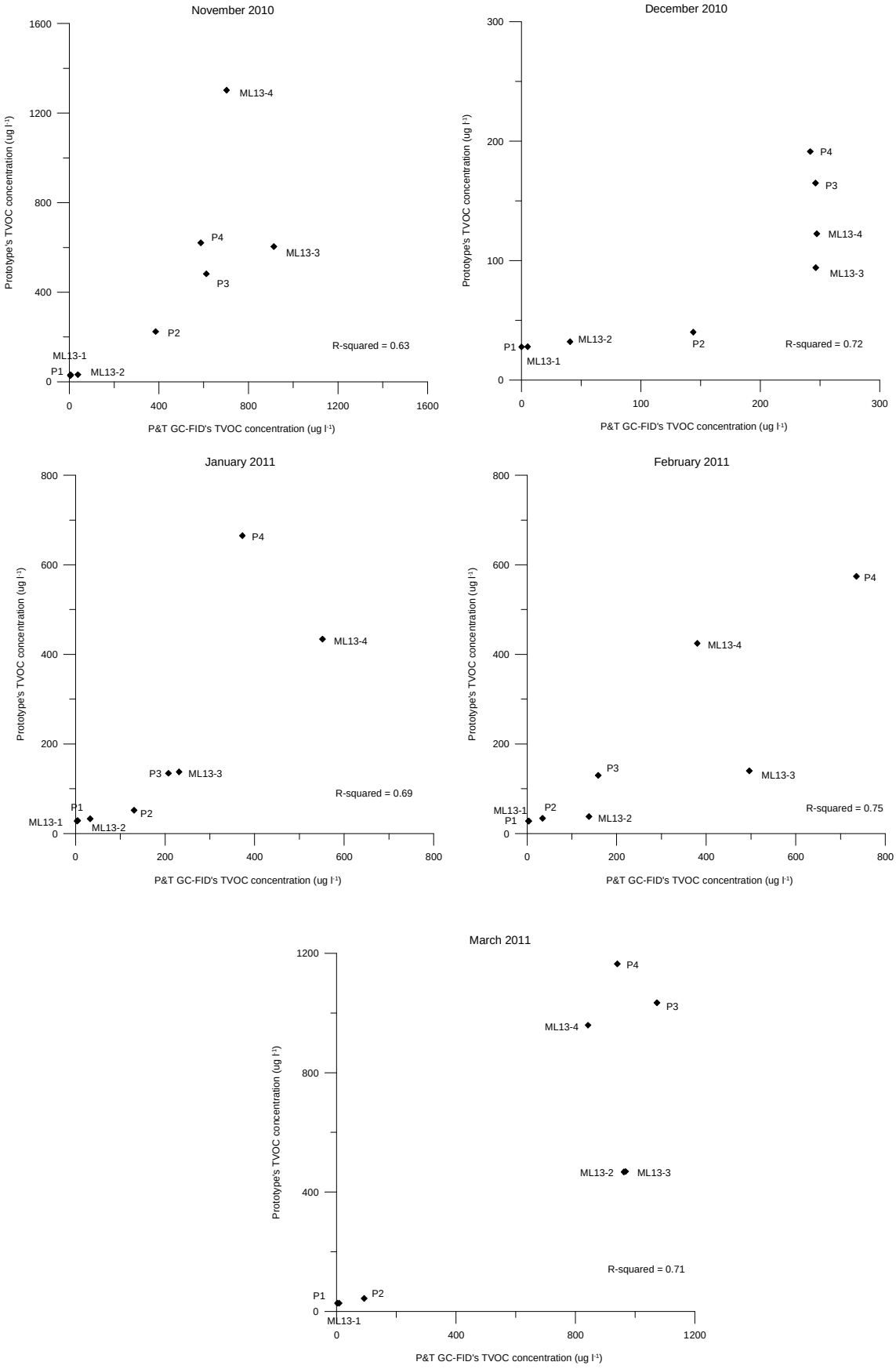

Figure 5.3 Plots of total VOC concentrations provided by P&T GC-FID data and measured by using the portable dissolved VOC detector for 5 different months

Month	Compound	P1 ($\mu g\ l^{-1}$)	P2 ($\mu g\ l^{-1}$)	P3 ($\mu g\ l^{-1}$)	P4 ($\mu g\ l^{-1}$)	ML13-1 ($\mu g\ l^{-1}$)	ML13-2 ($\mu g\ l^{-1}$)	ML13-3 ($\mu g\ l^{-1}$)	ML13-4 ($\mu g\ l^{-1}$)
November 2010	VC	0.00	6.30	26.50	49.00	0.00	0.26	30.20	129.00
	cis-DCE	0.09	125.00	238.00	316.00	0.09	3.83	439.00	522.00
	TCE	0.21	30.60	38.90	29.00	0.24	1.99	59.90	30.90
	PCE	4.11	224.00	309.00	193.00	5.05	32.00	384.00	20.30
December 2010	VC	0.00	0.24	10.52	30.14	0.00	0.72	7.76	21.22
	cis-DCE	0.00	14.64	82.45	183.26	0.74	6.23	73.85	171.20
	TCE	0.11	7.61	14.69	5.25	0.28	1.02	14.12	19.76
	PCE	0.00	121.36	138.59	23.16	4.12	32.73	150.79	35.11
January 2011	VC	0.00	1.32	12.18	46.61	0.00	0.29	10.82	113.75
	cis-DCE	0.00	34.80	72.88	267.90	0.00	3.75	90.14	397.39
	TCE	0.00	8.08	9.19	5.61	0.00	0.00	16.77	13.54
	PCE	3.58	86.51	113.40	52.54	4.50	28.62	113.62	27.01
February 2011	VC	0.00	0.97	9.59	129.62	0.00	9.57	39.08	78.03
	cis-DCE	0.00	10.24	64.93	564.18	0.00	62.92	239.46	261.15
	TCE	0.00	1.24	11.71	4.42	1.33	12.83	49.06	17.35
	PCE	2.79	21.74	72.46	37.43	2.57	52.74	168.56	23.34
March 2011	VC	0.00	1.98	144.89	265.23	0.00	19.45	17.19	182.16
	cis-DCE	0.00	33.25	616.45	639.88	0.00	437.89	415.28	605.77
	TCE	0.00	5.79	64.26	4.32	0.00	107.09	117.31	23.38
	PCE	2.69	51.24	247.72	31.04	7.87	398.14	418.32	31.01

Table 5.1 Individual concentrations measured by P&T GC-FID for every month

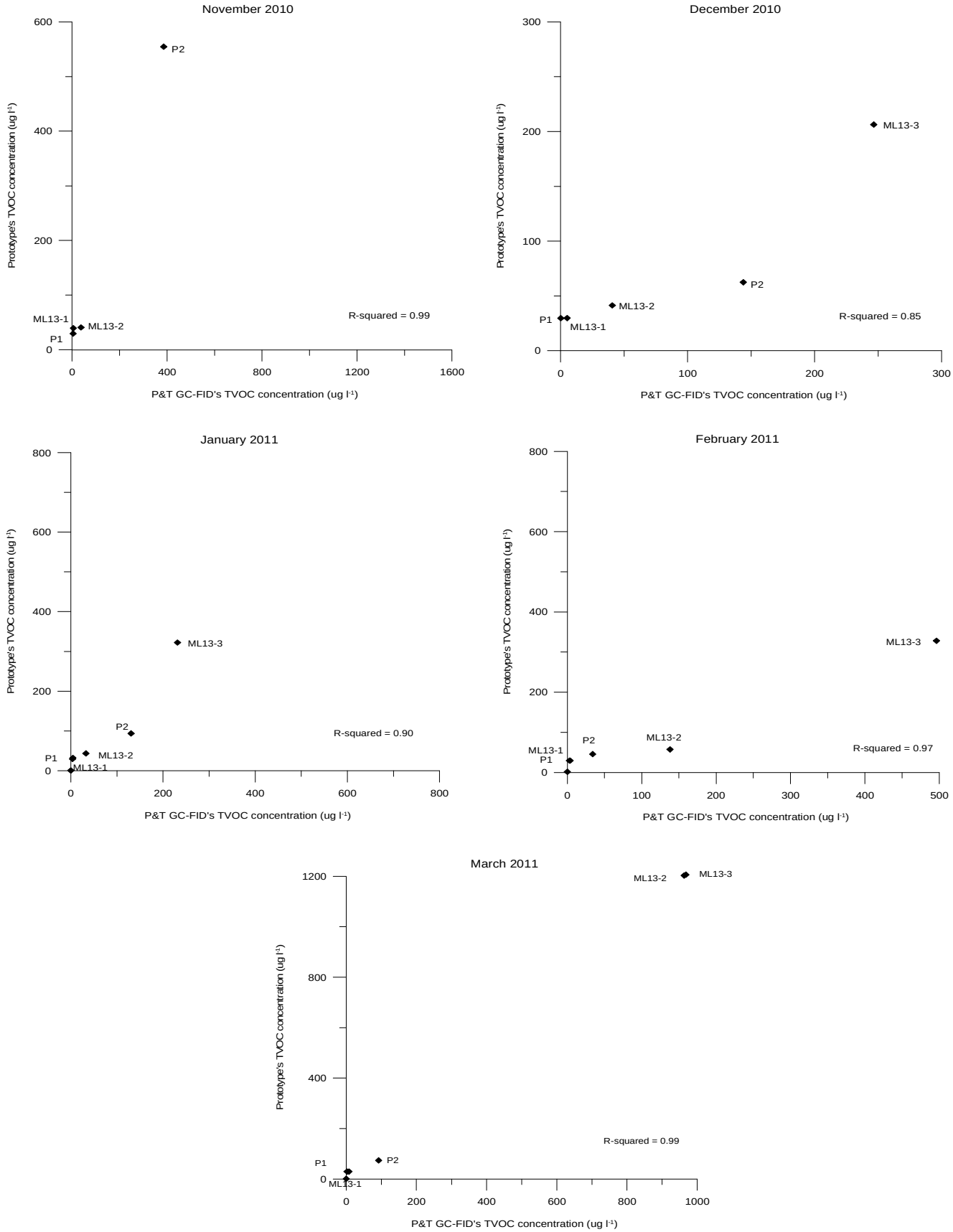

Figure 5.4 Plot of the total VOC concentration measured with the portable dissolved VOC detector and corrected for the effect of the temperature dependence of the Henry coefficient and the total concentration measured by P&T GC-FID data for 5 different months

5.3.2. Cost aspects

The more important objective for the development of an in – field VOC measurement instrument is the cost-effectiveness of the device. The expected total cost of the portable instrument amounts to 10.000 Swiss francs, estimating the parts' cost at 4.500 Swiss francs and labor's cost at 5.500. Additional costs should be taken into account for routine calibration, cleaning, battery charging or replacement of some components.

The number of samples that can be analyzed per day amounts to ten to twelve sampling points. The commercial analysis for chlorinated hydrocarbons per sample approaches to 120 Swiss francs. Consequently, after 8 days of field measurement, the investment in the portable instrument retaliates.

5.4. CONCLUSIONS

The portable dissolved VOC detector was used for a five - month period at a site contaminated by chlorinated hydrocarbons in Switzerland in parallel with laboratory analysis to prove its usability in the field. Results showed a correlation (R^2: 0.62 – 0.75) between the two approaches with laboratory concentrations being generally higher than *in situ* measurements. This difference is essentially caused by two factors: (1) the lower temperature of the groundwater relative to the laboratory conditions, which decreases Henry's coefficient and therefore constrains the molecular transfer to the gas phase; and (2) the presence at the field site of an additional compound (VC), which was not included in the initial mixture calibration, based on three common chlorinated hydrocarbons (*cis*-DCE, TCE and PCE). Correlation coefficients are improved (R^2 equal to 0.85-0.99) when the effect of the temperature dependence of the Henry's coefficient is taking into account for points where the VC concentration is not important. Further research is suggested to improve the prototype's reliability: (1) prototype's laboratory

experiments should be made with mixture's solutions containing VC and (2) at a temperature similar to field temperature.

Despite these factors which were not taken into account in these experiments, the portable detector is a flexible and promising approach for *in situ* dissolved VOCs analysis. In its current form, it enables the distinction between high-, medium-, and non-contaminated locations. Since a larger number of points can be measured in a relatively short period of time, and since results are immediately available unlike for conventional methods, it appears as a screening tool for site characterization and risk assessments.

CHAPTER 6

SUMMARY AND OUTLOOK

This study has developed and tested an *in situ* instrument for the determination of chlorinated hydrocarbons in groundwater. The two membrane materials considered in this study, polypropylene and PDMS, had different sorption and extraction properties which affected their suitability for the desired application. In order to determine the limiting factor of the mass transfer process for both membrane modules during the extraction of the organic compounds from water, the overall mass transfer coefficients, gas phase mass transfer coefficients and membrane mass transfer coefficients are calculated for each gas flow rate by using experimental results and the appropriate Sherwood correlations. A simple mathematical model has been presented to describe the mass transfer of the compounds through the hollow fiber membranes. This model was used to calculate the experimental overall mass transfer coefficients for both membranes during the membrane mass stripping method. For the PDMS module, the limiting factor was found to be the boundary layer in the aqueous phase. For the PP module, it was not clear which factor influences the overall mass transfer. The mass transfer through the PDMS membrane modules was better understood under the conditions tested, so it was chosen for the further experiments. Using the resistance in series model, the overall mass transfer coefficient was compared to the mass transfer coefficients estimated for the different layers (water boundary layer, membrane, gaseous boundary layer).

The transport mechanism for mass transfer across non-porous membranes is best described theoretically by the solution–diffusion model which consists of five steps: (1) diffusion from the bulk aqueous solution through a liquid boundary layer to the membrane surface, (2) sorption of the molecules in the membrane, (3) diffusion through the membrane and (4) desorption of the

molecules and (5) diffusion through the gas boundary layer outside the membrane where Henry's coefficient controls the relative concentration in the gas phase (relative to the equilibrium concentration). A higher value of the Henry's coefficient for a compound means that at near equilibrium, higher mass of this compound has to be transferred across the membrane to reach higher relative concentration in the gas phase. A more sophisticated model can be developed in the future, especially for the PDMS membrane module, which is the one selected for the further research.

A miniaturized photoionization detector was tested in this work for the analysis of the compounds in the gas phase as a composite index. In order to evaluate the overall performance of the detector, data on response curves, response time, stability, linearity and also influence of the gas flow rate and humidity were obtained. The detector has a large detection range from 5µg l^{-1} to 50mg l^{-1} and its response is very rapid. The detector showed a highly linear response over the full tested range, 10 – 500µg l^{-1}, and a good stability over time. However, a significant humidity effect was present.

A system developed with the combination of the PDMS hollow fiber membrane module and the miniaturized detector was tested for the sampling and analysis of the three chlorinated hydrocarbons (*cis*-DCE, TCE and PCE) in the laboratory and in the field. This prototype showed to have a detection limit of 20µg l^{-1} for a mixture of the compounds with a total precision of 10% for the mixture solution. This detection limit is lower that the Swiss legal limits according to OSites that apply downgradient of contaminated sites for TCE (70µg l^{-1}) and for PCE (40µg l^{-1}). The new device is suitable for monitoring chlorinated solvents in contaminated groundwater directly in the field.

The instrument was field tested at an ancient dry cleaner site in Switzerland during a five - month period. The tests show a good correlation between the field measurements and laboratory analysis when the effect of the temperature dependence of the Henry's coefficient was taken into

account for the points where VC's concentration was not important. The practical use of this device offers cost-effective and rapid on-site analysis even if some samples have to be taken for verification in the laboratory. The portable detector is a flexible and promising approach for *in situ* VOC measurements, which enables the distinction between high-, medium-, and low or non-contaminated locations. In its current form, it can be used as a screening tool for site characterization and risk assessment.

Due to the hydrophobic nature of the hollow fiber installed in the portable dissolved VOC detector and the relatively high gas-water partitioning of the VOCs, the instrument can be used for the analysis of other compounds with similar physicochemical properties as the three compounds tested here. For example, it is expected that benzene should have a lower detection limit that *cis*-DCE, TCE and PCE. But, its stabilization time should be longer than *cis*-DCE's and shorter than TCE's, as benzene's hydrophobicity is in the middle between these two compounds. In the case of measuring different organic compounds than these tested here, the instrument should be tested in the laboratory with the chosen compounds. The organic compounds to be analyzed have to be detectable by the PID detector. This method is not compatible for the analysis of the hydrophobic methane and freons.

This system is a screening tool for contaminated sites with the limitation of the concentration analysis of the organic compounds as a composite index. The two main disadvantages of the portable device are (a) the long stabilization time and so the measurement time and (b) the memory effects present related to the hollow fiber, so, a blank solution has to be pumped between two measurements, a subject that should be investigated in a more extended research. Currently, on-line continuous monitoring is limited by these memory effects. But, it could be a useful tool for detecting the location of the contamination source and the following up after site remediation.

While this work presents an interesting application of the portable device, further research should be done. A possible solution could be a heating chamber where the hollow fiber module can be put inside. A parallel temperature's increase with an air circulation through the membrane would accelerate the desorption of the molecules from the hollow fiber. In order to analysis each component separately and not as a composite index, the combination of the hollow fiber membrane module with another detector capable to identify the different compounds should be considered. An assessment for possible industrialization should be considered as a final step.

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