Novel passive sampling materials for the determination of priority pollutants in surface waters.

by

Rachel NicArdgháil

53345505

Thesis submitted for the Degree of Doctor of Philosophy

Supervisor: Prof. Fiona Regan

Dublin City University December 2011

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ACKNOWLEDGEMENTS

Firstly I'd like to thank Prof. Fiona Regan for giving me the opportunity to work within her research group in Dublin City University and for all her help within this project.

I would also like to thank all the friends I have made along the way both in my undergraduate degree who joined me in the undertaking of a PhD and also to the friends I made during my time as a postgraduate researcher. I want to make special mention of the friends I made within the group, both past and present; Lisa, Aga, James, Louise, Tim, Ciprian, Imogene and Li Li. They were there for me both with cups of tea and a friendly ear to chat to but also to help me when I needed it.

Thanks should be given to two fourth year students that I worked with, Helen Flynn and Niamh Nolan and also an exchange student Constance Balliet who worked with me over the summer of 2011 and was invaluable in the work carried out for the tuning of my passive sampling devices. Both Lorna Fitzsimons and Nina Hanzlikova deserve recognition for the help they provided me in determining the diffusion coefficients.

Finally, thanks to my parents, family and loved ones who have supported me not only through out the years but have been extremely helpful in the last few months helping to look after me and encouraging me during my worst moments.

This Project (Grant-aid Agreement No. 2007-PhD-ET-1) was carried out with the support of the EPA under the Science, Technology, Research & Innovation (STRIVE) Programme 2007 – 2013.

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ABSTRACT

The Water Framework Directive (WFD) is a European Union Directive which commits all European Union Member States to make all water bodies, inclusive of marine waters up to a kilometre from shore, of good status by 2015.

Since 2003 national regulations implementing the Directive have been put in place. There are 41 pollutants that were set down by the EPA as priority pollutants (Annex X of the WFD). Priority pollutants are specific pollutants that include heavy metals and specific organic chemicals. There are four main groups of priority pollutants; pesticides, metals and there compounds, polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds (VOCs). It is necessary to establish a monitoring system for priority pollutants that is not only cost and time effective but also simple to implement.

One emerging analytical method for the monitoring of these priority pollutants is the use of passive sampling devices. Passive samplers work on the basis of analyte diffusion into a membrane that is selective to their enrichment.

This thesis outlines the development of analytical methodology for the analysis of pesticides in aqueous solutions and also the development and screening of novel passive sampling materials.

The novel passive sampling polymer devices are made using poly(vinylchloride) (PVC) and contains a plasticiser to aid the enrichment of analytes. The passive sampling devices are exposed to aqueous systems spiked with priority pollutants for selected time periods. The analytes of interest are extracted from the passive samplers and the extracts are analysed using gas chromatography coupled with mass spectrometry (GC-MS).

ABBRIVIATIONS

a.m.u	Atomic mass units
AA	Annual Average
ASE	Accelerate Solvent Extraction
ATR	Attenuated Total Reflection
BHT	Butylated hydroxytoluene
BOP	Butyl Octyl Phthalate
CAS	Chemical Abstracts Service
DA	Diisononyl Adipate
DCM	Dichloromethane
DCU	Dublin City University
DDT	DichloroDiphenylTrichlorethane
DEHP	Diethyl Hexyl Phthalete
DMP	Dimethyl Phthalate
ECS	Electron Capture Detectors
EDC	Ethylene dichloride
EPA	Environmental Protection Agency
EQS	Environmental Quality Standards
EU	European Union
EVA	Ethylene Vinyl Acetate
FIFRA	Federal, Insecticide, Fungicide, and Rodenticide Act
FPD	Flame Photometric Detector
GC	Gas Chromatography
GC-MS	Gas Chromatography Mass Spectrometry
HCB	Hexachloro Benzene
HPLC	High Performance Liquid Chromatography
ICES	International Council for the Exploration of the Sea
IPA	Isopropyl Alcohol
k'	Capacity factor
LC	Liquid Chromatography

LC-MS	Liquid Chromatography Mass Spectrometry
LDPE	Low Density Polyethylene
LOD	Limit of Detection
LOQ	Limit of Quantification
MAC	Max Allowed Concentrations
MAE	Microwave Assisted Extraction
MAPS	Membrane Assisted Passive Sampler
MCPP	Methylchlorophenoxypropionic acid
ML	Methyl Laurate
MS	Mass spectrometry
NPD	Nitrogen-Phosphorus Detector
NPLC	Normal Phase Liquid Chromatography
OSPAR	Convention for the Protection of the Marine Environment of the North-East Atlantic
PAH	Polycyclic Aromatic Hydrocarbons
PCB	Polychlorinated biphenyls
PDMS	Polydimethylsiloxane
phr	Parts per hundred of resin
PISCES	Passive In-Situ Concentration Extraction Sampler
POCIS	Polar Organic Chemical Integrative Sampler
POP	Persistent Organic Pollutants
PRC	Performance Reference Compounds
PTFE	Polytetrafluoroethylene
PVC	Poly (VinylChloride)
R.T.	Retention Time
RBMP	River Basin Management Plans
RPLC	Reversed Phase Liquid Chromatography
RSD	Relative Standard Deviation
SAW	Surface Acoustic Wave
SFE	Supercritical Fluid Extraction
SIM	Selected Ion Monitor

SPE	Solid Phase Extraction
SPMD	Semi-permeable membrane devices
SPME	Solid Phase Micro Extraction
SRM	Selected Reaction Monitor
Std Dev	Standard Deviation
SWIFT	Screening methods of Water data InFormation
Tg	Glass transition temperature
THF	Tetrahydrofuran
TIE	Tosicity Identification Evaluate
TWA	Time Weighted Average
US	United States
VCM	Vinyl chloride monomer
VOC	Volatile Organic Compounds
WFD	Water Framework Directive
α	Relative retention time

CHAPTER 1: INTRODUCTION

1.1 INTRODUCTION

The majority of aquatic monitoring programmes rely on the collection of discrete grab, spot or bottle samples at any given time and place (1). These approaches may be suitable for the identification of episodic events but are not as effective when the pollutants are only present in the water at trace levels since large volumes of water are needed for the analysis (2). This method then tends to be cumbersome, and both cost and time ineffective before the analysis results are obtained.

With grab sampling, it is also not always possible to fully assess the bio-available fraction of the target analytes. This can be relevant for the prediction of the risk factors involved for the analytes in the environment, due to the fact that grab sampling is related to specific place and time. The results obtained are not always representative for the whole area sampled (3). With all these factors in mind it can be noted that more representative monitoring methods are needed. Some alternative methods that are used for aquatic monitoring are increasing the frequency of the sampling, automatic sequential sampling (4), and continuous on line monitoring systems, which can be expensive to implement.

Passive sampling is now recognised as a promising technique for analysis (2), (5), (6), (7), involving the measurement of analyte concentration as a time weighted average (TWA) and shows promise as a current and future tool for the quantitative monitoring of pollutants in the environment.

1.1.1 AIMS AND OBJECTIVES

The work presented within this thesis will show the development and tuning of both methods for priority pollutant detection and also the development of novel passive sampling devices that can be deployed in aid to meet the requirements set down by current legislation.

Chapter 1 outlines the legislation that is both previously and currently enacted into European Law. Under this legislation there is a need for more regular sampling data to be obtained. One alternative method to the current grab sampling technique implemented is the use of passive sampling devices. The theory behind passive sampling is detailed, and current commercial passive sampling devices are described, alongside issues that may arise through their usage.

Chapter 2 describes the development and validation of methods that can be used for analysis of priority pollutants. The methods described are solid phase extraction for the clean-up and pre-concentration of water samples; gas chromatography-mass spectrometry method used for the analysis and analyte determination of water samples and exposed passive samplers. A high performance liquid chromatography method was also developed to aid in the rapid determination of test analytes during the development stage of the novel passive samplers.

The development of novel passive sampling devices is detailed within Chapter 3. Within this work the selection of plasticiser, extraction solvent and casting method is discussed. These developed samplers were then exposed to a series of chemicals within laboratory conditions and their diffusion profiles both in single and multi component mixtures are detailed. The effect the plasticiser has on the uptake rate of chemicals into the novel passive sampling device was also studied. A selection of 30 forms of the novel passive sampling devices were tested against three compounds and tested on basis of enrichment and pre-concentration of analytes. Out of this selection three sampler configurations were looked at in more detail.

Chapter 4 detailed work carried out on the enrichment of priority pollutants into novel plasticized membranes using Attenuated Total Reflection (ATR) spectroscopy. These experimental values were then used to calculate the diffusion coefficient of priority pollutants using Matlab.

Deployment of the novel passive sampling devices developed in Chapter 3 is described in Chapter 5. The novel samplers were deployed at two distinct sites; Lough Hyne, Co Cork for one month, and Ringsend, Co. Dublin over a period of 6 months. For the last month of deployment commercial samplers were also tested against the developed sampers in Ringsend.

This chapter shows a brief overview of the legislation in relation to environmental issues and how the WFD (2000/60/EC) was enacted into European Law. Within this directive there are 41 priority pollutants mentioned in Annex X. Priority pollutants are substances which are toxic, persistent in the environment and can become bio-available to mammals. Within this chapter priority pollutants are divided into four groups; pesticides, metals and trace elements, volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs), for ease of discussion.

Within the WFD, a monitoring scheme has been outlined which includes more frequent analyses of surface waters than previously carried out. Due to this it is important that less expensive and less time consuming methods of analysis are developed and validated. The most commonly used method of analysis currently is grab sampling however a new method of sampling, passive sampling, shows great promise for determination of TWAs of pollutants, which will also include episodic events that could easily be missed by traditional grab sampling.

1.2 LEGISLATION

Within the European Union, it is possible to divide EU environmental and water policy into three main time periods (8). The initial time period was from 1973 to 1986 and incorporated the initial three environmental programmes. During this period in environmental policy the focus was on ‘water use’ directives and ‘water pollutant’ directives. ‘Water use’ directives included Drinking Water (75/400/EEC), Bathing Water (76/160/EEC) and Fish (78/659/EEC) and Shellfish Harvesting (79/923/EEC) legislation. ‘Water pollutant’ directives regulated the allowable levels of discharge in relation to specific pollutants. The two key ‘water pollutant’ directives during this time were for the emission of Dangerous Substances to surface (76/464/EEC) and ground water (80/68/EEC) bodies.

The Oslo Convention came into force in 1974 with the main aim of regulating dumping operations that involved industrial waste, dredged material and sewage sludge. In 1978 the Paris Convention came into force with the primary focus being in the prevention and reduction and, if needed, the elimination of pollution in the

Convention area from land based sources, which can be discharged into rivers, pipelines and also the atmosphere (9). Neither of the above conventions adequately controlled the many sources of pollution and the adverse effects of human activities upon the environment. This resulted in an amalgamation of the two conventions creating the Convention for the Protection of the Marine Environment of the North-East Atlantic or OSPAR (10). Ireland is a contracting party to OSPAR and reports annual environmental data to the International Council for the Exploration of the Sea (ICES) database for selected pollutants. The OSPAR priority pollutant list played an important role during the selection of the priority substances for the WFD, with the final list resulting in 41 priority substances (11).

The second period occurred between 1987 and 1992 and during this time there was assignment of a European competence for a common environmental policy. Two new directives were introduced to tackle the main sources of water quality deterioration; pollution from urban waste water (91/271/EEC) and pollution from nitrates from agricultural run-off (91/676/EEC).

The third period in EU water regulation is currently underway (1992-present day). During this period the two main documents of legislation are The Drinking Water Directive (98/83/EC) and The Water Framework Directive (2000/60/EC). The new Drinking Water Directive has several parameters altered from the previous directive (80/778/EEC). Member States have now added parameters such as magnesium, total hardness, phenols, zinc, phosphates, calcium and chlorite. This updated Directive states that member states are required to regularly monitor the quality of water that is intended for human consumption, through use of methods stated in the directive or other equivalent methods. Under this directive member states must publish drinking water quality reports every three years and the European Commission then publishes a summary report. The WFD is explained in more detail in section 1.2.1.

1.2.1 WATER FRAMEWORK DIRECTIVE

The Water Framework Directive (WFD, 2000/60/EC) was introduced not only to protect but also improve the quality of all water bodies at river basin level throughout Europe (11). The WFD was adopted in 2000 as a single piece of legislation covering rivers, lakes, groundwater and transitional (estuarine) and coastal waters. The directive affects 27 countries and marks an important trend towards an ecosystem based approach for water policy and resource management. The WFD's aims are to ensure the 'good' status of all water bodies up to a kilometre from shore by 2015 (12). An important goal is that there is no deterioration of either chemical or biological good status upon the implementation of measures within the WFD (8). The WFD also has several other well defined objectives such as to promote sustainable water use, to enhance protection and improvement of the aquatic environment for the progressive reduction of discharge and to contribute to mitigating the effects of floods and droughts (12).

The EU's WFD is one of the most important pieces of environmental legislation that has been produced in recent years and is likely to transform the way that water quality monitoring will be undertaken across all member states (13). Its aim is to complement a number of other existing legislative instruments some of which include the Bathing (76/160/EEC), Drinking (98/83/EC), Fish (78/659/EEC) and Shellfish (79/923/EEC) Water Directives, along with those based on specific substances or sources of pollution (i.e. Dangerous Substances (76/464/EC), Groundwater (80/68/EEC), Nitrate (91/676/EEC) and Pesticide (91/414/EEC) Directives (14). The term 'water' within the WFD encompasses most water body types, so the legislation covers not only groundwater, but also all coastal and surface waters up to one kilometre from shore.

The WFD has long term objectives as well as short term ones, with some of the long term being over a period of 25 years. There are some important milestones along the way: (a) In 2009 - the adoption of river basin management plans, which includes a program of measures stating how the relevant environmental objectives are to be achieved (Article 11 and 13 WFD) (b) The achievement of good status of water bodies by 2015. After this time new management plans are set to be devised and every six years exemptions will be revised (15). As of 11th April 2011, 20 member states have adopted River Basin Management plans, 3 member states (Cyprus, Denmark and Slovenia) have finalised the river basin management plans but are awaiting adoption and 4 member states (Belgium, Greece, Portugal and Spain) have either not started consultation or consultation is currently ongoing (16).

Article 16 of the WFD sets out EU strategies against the pollution of water which states that the commission shall review the list of priority substances (Annex X) at a minimum of once every four years (17). This list consists of mainly organic contaminants (e.g. pesticides, hydrocarbons, and organic solvents) but also included in the list are four toxic metals and their compounds and one organo-metallic compound (18).

Article 8 (1) of the directive states: 'Member states shall ensure the establishment of programmes for the monitoring of water status in order to establish a coherent and comprehensive overview of water status within each river basin district'.

Monitoring is required to cover a number of 'water quality elements' (20) including physiochemical measurements, for example temperature, density, colour, pH value, and turbidity; biological elements looking at the distribution and composition of the species and biological effects; and chemical monitoring is also expected to intensify and will follow a list of priority chemicals (inorganic and organic pollutants and substances) that will be reviewed every four years (19). Environmental quality standards (EQSs) were proposed for the 33 priority substances mentioned in Annex X of the WFD in July 2006, at this time EQSs were also proposed for the remaining 8 pollutants mentioned in (76/464/EEC). Quality standards were published in December 2008 (1008/105/EC) with 41 substances named, amending the Water Framework Directive (2000/60/EC).

The WFD has set out three different types of monitoring programmes, as outlined below:

Surveillance Monitoring: was designed to provide information to assess long term changes in natural conditions of as a result of anthropogenic activity (20). The data obtained from this was collected over a twelve month period, and provided the basis for the production of river-basin management plans (RBMPs) to be published by December 2009. Priority substances are of particular importance in surveillance monitoring.

Operational monitoring: aimed to provide information that could be further used to classify the status of water bodies that were at risk of failing their environmental objectives (23). This was also useful when measures were taken in the improvement of water quality, whereby it was possible to assess any changes that resulted from these actions. Operational monitoring is obviously required where pollution or other impacts on ecological status are apparent.

Investigative Monitoring: was designed to assess the impact of accidental pollution events and also to serve as a follow up to surveillance monitoring, when it was shown that environmental objectives for specific water bodies were not likely to be met. The investigative monitoring programme includes snapshot monitoring programmes. Also included within the investigative monitoring subnet are electronic alert networks aimed at providing greater temporal resolution to ascertain of the causes and likely sources of pollution.

Previous monitoring programs have generally been based on the collection of spot samples. There are drawbacks to this type of sampling method, especially in cases where the samples are being taken from environments where the concentration of the analytes can vary significantly over time, e.g. pesticides, and also where there are possibilities of intermittent pollution events (21). For spot sampling the analysis will only provide data for the pollutants at that given time and place, and for the determination of a TWA a large number of samples would need to be collected (22). Passive sampling methods can allow for both the control and reproducibility offered by grab sampling, and time integrated results offered from biota and sediment samples. One advantage of passive sampling over spot (grab) sampling is that for the duration of the sampling only one device is needed and this device will give a TWA concentration of analytes within the sampled area. Where only trace levels of the pollutants are present, large volumes of water would need to be analysed to determine the concentration for spot sampling (23) whereas one passive sampling device could determine the TWA with shorter analysis time.

In 2010 De Stefano (24) undertook a study to assess the quality of stakeholder participation at the start of the WFD implementation. It showed that by 2003 there were positive results in several of the 27 countries but that there would need to be significant efforts to improve these results throughout Europe. The results were broken down into three main sections; Proactive Information, Public Consultation, and Active Involvement.

It was found that proactive information was heterogeneous throughout Europe, however, it should be noted that the countries that showed moderate to poor compliance (e.g. Turkey, Italy, Poland etc.) outweighed countries with good compliance (e.g. Finland, Sweden, France etc.). For public consultation a clear division between Northern and Central Europe (high levels of compliance) and Eastern and Southern Europe (poor compliance) was observed. With respect to active involvements across Europe none of the countries looked at were classified as ‘very good’, and one third of these countries showed low levels of compliance in this issue.

The Screening methods of Water data InFormaTion (SWIFT-WFD) project was set up by the European Commission (EC) (Contract no: SSPI-CT-2003-502492) and ran from January 2004 until March 2007 (25). SWIFT-WFD was set up to support the successful implementation of the WFD (20), as it would need quality water data that could be comparable to a series of different water bodies.

SWIFT-WFD identified the main chemical and biological monitoring tasks within the WFD (26), and focused on the use of the classical chemical monitoring methods for trace level pollutants for subsequent environmental quality standards (EQS) focussed compliance tests (27). A set of tools was then proposed to rise to the challenges and environmental objectives faced, that the traditional monitoring techniques were unable to achieve. Once this was completed, selected results from within the SWIFT-

WFD field trial were presented as case studies and used to demonstrate the usefulness of some of these tools. It was found that the Ecoscope sampler could be used for the tracing of point or diffuse sources of contaminants (11), that it was possible to obtain TWA measurements of labile concentrations of heavy metals by using the Chemcatcher passive sampler. Through the use of a selection of these tools an informative picture of the chemical status of the water can be maintained (19).

1.3 PRIORITY POLLUTANTS

There are many organic compounds that can be released into the environment that will be degraded effectively, however there are some compounds that show more persistence and can be distributed over large water areas with the further possibility of accumulation into organisms within the environment. Priority or hazardous compounds can be defined as compounds (or groups thereof) that are persistent, toxic and liable to bio-accumulate, or that give equivalent level of concern, for example, through degradation into hazardous substances (28) (29). The four main characteristics of priority pollutants are that they are toxic, persistent in the environment, their semi-volatile nature to be bio-available to mammals, and are also capable of travelling great distances (30). The compounds would show strong indications of risks in the marine environment and have a potential threat to human health with the consumption of affected seafood (31).

For substances occurring naturally, or produced through natural processes, such as cadmium, mercury and polycyclic aromatic hydrocarbons (PAHs), complete phase-out of emissions, discharges and losses from all potential sources is impossible. When the relevant individual directives are drawn up, this situation must be properly taken into account and measures should aim at the cessation of emissions, discharges and losses into water of those priority hazardous substances which derive from human activities (32).

Below (Table 1.1) the annual average concentrations (AA) as well as the max allowed concentrations (MAC) for the priority pollutants are outlined for the priority pollutants mentioned in Annex X of the WFD (33). The AA refer to the average concentrations found in surface water by the Irish EPA during a monthly monitoring programme (May 2005 - October 2006) across sites that were spread across Ireland.

Table 1.1: Showing the AA concentration and MAC in surface waters as given by the Irish EPA. AA concentrations were calculated between May 2005 and October 2006 at a series of sites across the island of Ireland (33).

		Annual Average Concentration (μgL^{-1})		Maximum Allowed Concentration (μgL^{-1})	
		AA freshwaters	**AA marine**	**MAC freshwaters**	**MAC marine**
Alachlor	159772-60-8	0.3	0.3	0.7	0.7
Anthracene	120-12-7	0.1	0.1	0.4	0.4
Atrazine	1912-24-9	0.6	0.6	2	2
Benzene	71-43-2	10	8	50	50
Pentabromodiphenlyether	32534-81-9	0.0005	0.0002	n/a	n/a
Cadmium and its compounds	7440-43-9	0.08-0.25	0.2	0.45-1.5	
C10-13-Chloroalkanes	85535-84-8	0.4	0.4	1.4	1.4
Chlorfenvinphos	470-90-6	0.1	0.1	0.3	0.3
Chlorpyrifos	2921-88-2	0.03	0.03	0.1	0.1
1,2-Dichloroethane	107-06-2	10	10	n/a	n/a
Dichloromethane	75-09-2	20	20	n/a	n/a
DEHP	117-81-7	1.3	1.3	n/a	n/a
Diuron	330-54-1	0.2	0.2	1.8	1.8
Endosulfan	115-29-7	0.005	0.0005	0.01	0.004
Fluoranthene	206-44-0	0.1	0.1	1	1
Hexachlorobenzene	118-74-1	0.01	0.01	0.05	0.05
Hexachlorobutadiene	87-68-3	0.1	0.1	0.6	0.6
Lindane	608-73-1	0.02	0.002	0.04	0.02
Isoproturon	34123-59-6	0.3	0.3	1	1
Lead and its compounds	7439-92-1	7.2	7.2	n/a	n/a
Mercury and its compounds	7439-92-1	0.05	0.05	0.07	0.07

Naphthalene	91-20-3	2.4	1.2	n/a	n/a
Nickel and its compounds	7440-02-0	20	20	n/a	n/a
Nonylphenols	25154-52-3	0.3	0.3	2	2
Octylphenols	1806-26-4	0.1	0.01	n/a	n/a
Pentachloro-benzene	608-93-5	0.007	0.0007	n/a	n/a
Pentachlorophenol	87-86-5	0.4	0.4	1	1
PAHs	n/a	n/a	n/a	n/a	n/a
(benzo-a-pyrene)	50-32-8	0.05	0.05	0.1	0.1
(benzo-b-fluoranthene)	205-99-2	∑=0.03	∑=0.03	n/a	n/a
(benzo-k-fluoranthene)	207-99-2			n/a	n/a
(benzo-k-fluoranthene)	207-08-9	∑=0.002	∑=0.002	n/a	n/a
(benzo-g,h,i-perylene)	191-24-2			n/a	n/a
(indeno(1,2,3-cd)pyrene)	191-39-5			n/a	n/a
Simazine	122-34-9	1	1	4	4
Tributyltin	688-73-3	0.0002	0.0002	0.0015	0.0015
Trichlorobenzene (all isomers)	12202-48-1	0.4	0.4	n/a	n/a
Trichloromethane	67-66-3	2.5	2.5	n/a	n/a
Trifluarin	1582-09-8	0.03	0.03	n/a	n/a
Dichloroiphenyltrichloroethane total	n/a	0.025	0.025	n/a	n/a
para-para DDT	50-29-3	0.01	0.1	n/a	n/a
Aldrin	309-00-2	∑=0.010	∑=0.005	n/a	n/a
Endrin	60-57-1			n/a	n/a
Dieldrin	72-20-8			n/a	n/a
Isodrin	465-73-6			n/a	n/a
Carbontetrachloride	56-23-5	12	12	n/a	n/a
Tetrachloroethylene	127-18-4	10	10	n/a	n/a
Trichloroethylene	79-01-6	10	10	n/a	n/a

For the purposes of this project the 41 priority substances have been broken down into four groups, based on their application and chemical and physical properties.

Out of the four groups, pesticides, polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs) and metals and their trace elements, two groups are detailed below (section 1.3.1 and section 1.3.2).

Within these tables selected physical and chemical data for the priority substances are outlined. These include the Chemical Abstracts Service number, (CAS) which is an unique numerical identifier that is assigned to each chemical that has described in scientific literature. The molecular formula which is a means of expressing information about the atoms that constitute a particular chemical compound, the molecular weight which is the mass of one molecule of the analyte in atomic mass units (a.m.u.), and finally the Log K_{ow} value.

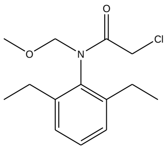
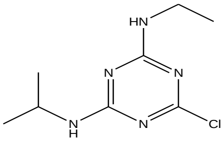
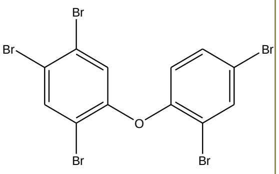
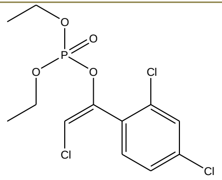
The values for K_{ow} are most often expressed on a log basis due to the fact that measured values range from 10^{-3} to 10^{7}, Log K_{ow} is also termed the octanol-water partition coefficient and it is a measure of the equilibrium concentration of a compound between octanol and water. From this value, in the range of -3 to 7 for the majority of compounds, you can deduce if a compound will preferentially partition into soil organic matter instead of water. This can be an important factor in the monitoring of selected pollutants. It is important not just to analyse the concentration of the analyte in the water, as this only related to the dissolved fraction, but to also determine the concentration of the analyte in sediment.

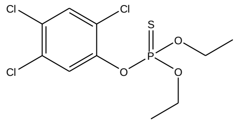
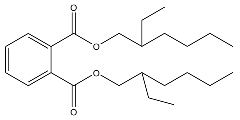
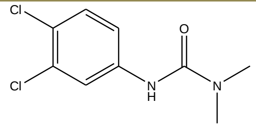
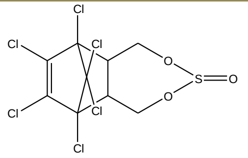
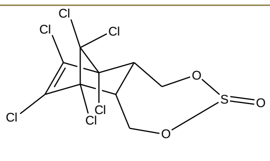
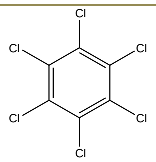
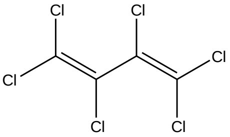
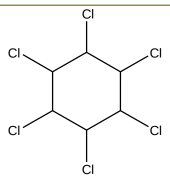
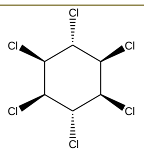
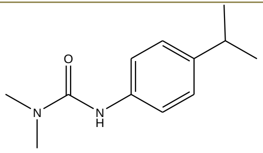
1.3.1 PESTICIDES

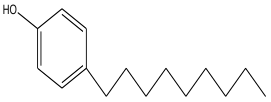
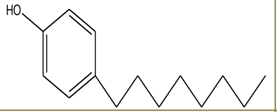
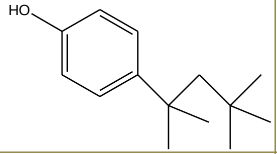
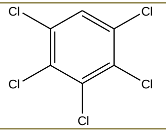
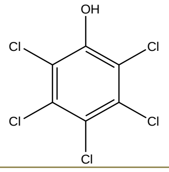
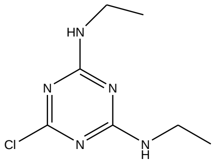
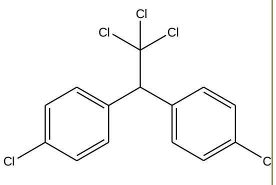
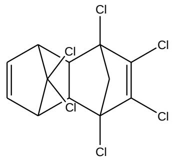
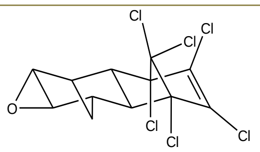
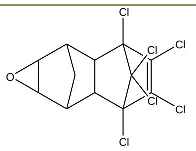
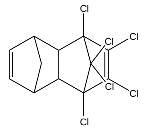
Pesticides have been used extensively since the nineteenth century with sulphur compounds finding use as fungicides. Later in the nineteenth century, for control of insects that would attack fruit and vegetable crops, arsenic compounds were introduced. In the 1940s (34) more synthetic compounds were introduced, most notably dichlorodiphenyltrichlorethane (DDT) (35).The majority of chemicals mentioned in Annex X of the WFD can be classed as pesticides. Pesticides have been broadly defined by the United States FIFRA (Federal, Insecticide, Fungicide, and Rodenticide Act) as any substance or mixture of substances that are intended to prevent, destroy, repel or mitigate pests including insects, rodents and weeds (36). According to Tomlin (37) there are over 800 compounds applied to agricultural crops to control or destroy molds, insects and weeds. In the past the usage of pesticides was considered a good sign of progress in agricultural production, however in more recent times it has been seen that pesticides can move through air, soil and water and find their way into living tissue when they can undergo biological magnification.

Within the group of pesticides it is possible to have sub-groups; main ones of which include organochlorines, organophosphates and carbamates, with the organochlorines being predominately replaced with the latter two groups.

Table 1.2: Table of pesticides mentioned in Annex X of the WFD with selected physical and chemical information (Log K_{ow}, M. Weight, M. Formula and structures)

CAS Number	Priority Substance	Structure	M. Weight ($gmol^{-1}$)	M. Formula	Log K_{ow}
15972-60-8	Alachlor		269.77	$C_{14}H_{20}ClNO_2$	3.5
1912-24-9	Atrazine		215.68	$C_8H_{14}ClN_5$	2.61
32534-81-9	Brominated diphenylethers		564.69	$C_{12}H_5Br_5O$	5.03-8.09
470-90-6	Chlorfenvinphos		359.57	$C_{12}H_{14}Cl_3O_4P$,	3.82

2921-88-2	Chlorpyrifos		350.59	$C_9H_{11}Cl_3NO_3PS$	5.27
117-81-7	Di(2-ethylhexyl) phthalate (DEHP)		390.54	$C_{24}H_{38}O_4$	7.5
330-54-1	Diuron		233.09	$C_9H_{10}Cl_2N_2O$	2.67
115-29-7	Endosulfan		406.93	$C_9H_6Cl_6O_3S$	3.5
959-98-8	α-endosulfan		406.93	$C_9H_6Cl_6O_3S$	3.83
118-74-1	Hexachloro benzene		284.8	C_6Cl_6	5.31
87-68-3	Hexachloro butadiene		260.76	C_4Cl_6	4.78
608-73-1	Hexachloro cyclohexane		290.83	$C_6H_6Cl_6$	α - 3.8; β -3.78; δ - 4.14
58-89-9	(γ isomer, Lindane)		290.83	$C_6H_6Cl_6$	3.9
34123-59-6	Isoproturon		206.28	$C_{12}H_{18}N_2O$	2.84

104-40-5	(4-(para)-nonylphenol)		220.35	$C_{15}H_{24}O$	5.76
1806-26-4	Octylphenols		206.32	$C_{14}H_{22}O$	5.14
140-66-9	(para-tert-octylphenol)		206.32	$C_{14}H_{22}O$	3.7
608-93-5	Pentachloro benzene		250.34	HC_6Cl_5	5.17
87-86-5	Pentachloro phenol		266.34	C_6Cl_5OH	5.2
122-34-9	Simazine		201.66	$C_7H_{12}ClN_5$	2.4
50-29-3	para-para-DDT		354.49	$C_{14}H_9Cl_5$	6.36
309-00-2	Aldrin		364.91	$C_{12}H_8Cl_6$	6.1
60-57-1	Dieldrin		380.91	$C_{12}H_8Cl_6O$	5.4
72-20-8	Endrin		380.91	$C_{12}H_8Cl_6O$	5.2
465-73-6	Isodrin		364.91	$C_{12}H_8Cl_6$	5.32

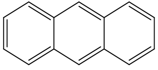
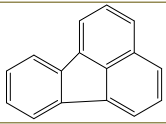
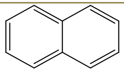
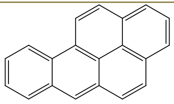
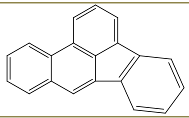
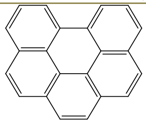
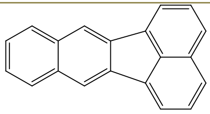
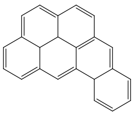
In the report published by the Department of Agriculture, Fisheries and Food (38) there is a list of plant protection products that are registered in Ireland as of January 2nd for the year in question (in this case 2011). These products outline the active ingredient, concentration levels and the company which holds the authorization to produce the products. Within the list of active substances that have been approved for use in plant protection products (and also included in Annex I of 91/414/EEC) were two pesticides that are seen in the above table (Table 1.2). These pesticides were isoproturon and chlorpyrifos and both were available for professional usage. Isoproturon was registered in three different formulations with concentrations vari from 125 – 500 gL^{-}1 and marketed by Farmco Agritrading Limited, Nufourmilk Ltd and BASF Ireland Ltd under the trade names of FARMCO Autumn Herbicide, Fieldguard and Encor respectively. Chlorpyrifos was available in two formulations both at 480 gL^{-1} and marketed by Dow AgroSciences and Unichem Ltd.

These were the only two exceptions made and many of the other pesticides mentioned above (Table 1.2) are listed under active substances that had been refused approval where a decision had been made not to include them in Annex I of Directive 91/414/EEC on 1/1/11.

1.3.2 POLYCYCLIC AROMATIC HYDROCARBONS

Polycyclic Aromatic Hydrocarbons (PAHs) are a class of organic compounds that have two or more fused benzene rings, consisting of only carbon and hydrogen. The principal sources of PAHs in the atmosphere are combustion of fossil fuels in heat and power generation, refuse burning and coke ovens (39). PAHs do not degrade easily under natural conditions, and there is a link between increased persistence with increased molecular weights (40).

Table 1.3: Table showing PAHs mentioned in Annex X of the WFD with selected physical and chemical information (Log K_{ow}, M. Weight, M. Formula and structures)

CAS number	Priority Substance	Structure	Molecular Weight $(gmol^{-1})$	Molecular Formula	Log K_{ow}
120-12-7	Anthracene		178.23	$C_{14}H_{10}$	4.54
206-44-0	Fluoranthene		202.25	$C_{16}H_{10}$	4.7
91-20-3	Naphthalene		128.17	$C_{10}H_8$	3.3
50-32-8	Benzo (a) pyrene		252.31	$C_{20}H_{12}$	5.97
205-99-2	Benzo (b) fluoranthene		252.31	$C_{20}H_{12}$	5.78
191-24-2	Benzo (g,h,i) perylene		276.33	$C_{22}H_{12}$	6.63
207-08-9	Benzo(k)fluoranthene		252.31	$C_{20}H_{12}$	C_{18}: 5.6; C_{20}: 6.11
193-39-5	Indeno(1,2,3-cd)pyrene		276.33	$C_{22}H_{12}$	$C_{22}H_{11}$:6.8 $C_{22}H_{12}$: 7.12

1.4 PASSIVE SAMPLING

1.4.1 HISTORICAL PERSPECTIVE

Passive sampling, which has also been referred to as passive dosimetry, is a recent technique for the determination of pollutants in aquatic environments (7). Passive sampling works on the principle of the free flow of the analyte molecules from a sampled medium to a collecting medium based on a result of chemical potential differences (5). Before the late 1980's the study of passive sampling was contained mainly to gas and air sampling, and in 1987 the first publication on a passive sampler for organic micro-pollutants in water was published. It was not until the 1990's that there was a dramatic increase in the publications as can be seen below (Figure 1.1) (41). This increase came about once the sensitivity of the passive sampler was published as being able to detect compounds in water at pgL^{-1} levels (42) (43), and from this point on there has been a dramatic increase in interest within this field.

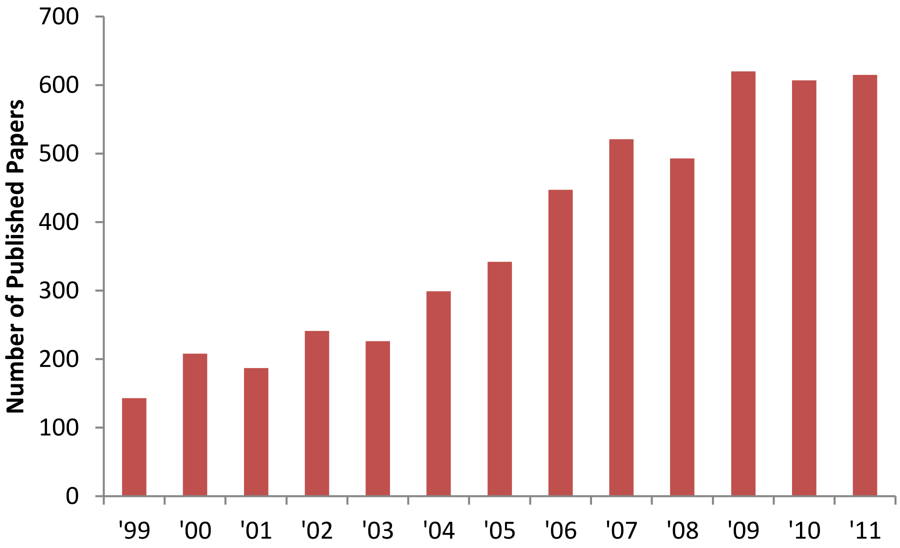


Figure 1.1: Statistics for the number of articles published on applications of passive sampling devices in the years between January 1999 and mid December 2011 (from an advanced search on Google Scholar for "Passive Sampling")

As can be seen from the above figure (Figure 1.1) the growth of passive sampling in research has developed in the past decade and is now widely used in the pollution monitoring of many different types of environments, e.g air and water.

There are some methods, that attempt to overcome problems which are associated with spot sampling, for example online continuous monitoring, bio-monitoring and passive sampling. Out of the methods just mentioned, passive sampling technology has the greatest potential to become a reliable, robust and cost effective tool that could be used for monitoring programmes throughout Europe.

1.4.2 THEORY

In a 2002 review, Górecki and Namicśnik defined passive sampling as "any sampling technique based on free flow of analyte molecules from the sampled medium to a collecting medium, as a result of a difference in chemical potential of the analyte between the two media" (5).

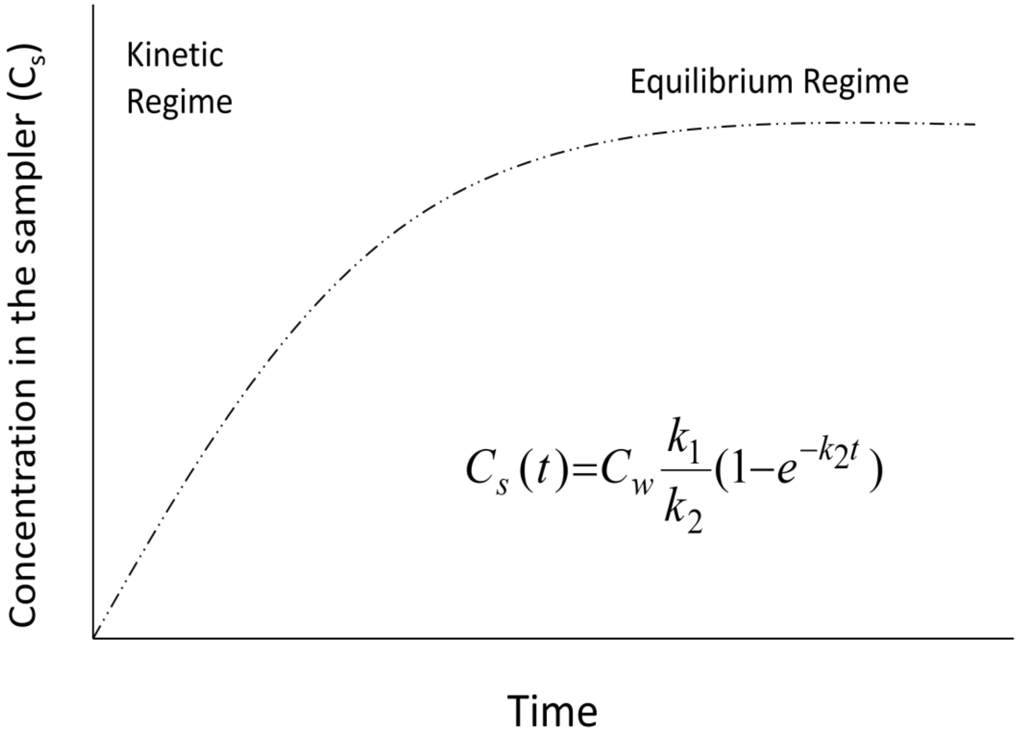


Figure 1.2: Exchange kinetics between the sampler and the water (Graphic adapted from Vrana *et al.* (16)). Both regimes observed during a passive sampling deployment are also shown (kinetic and equilibrium)

Sampling is able to proceed with no energy source due to the difference in chemical potentials of the sampled pollutants. The uptake of the pollutants into the sampler will also depend on environmental conditions, the design of the sampler, and the physical chemical properties of the pollutants (44).

In aquatic passive sampling a receiving phase is exposed to the water phase, without aiming to quantitatively extract the dissolved contaminants. All passive sampling devices absorb/adsorb pollutants from water as shown above (Figure 1.2). The exchange kinetics between a passive sampler and water phase can be described by a first order, one compartment mathematical model based on Equation 1.1.

$$C_s(t) = C_w \frac{k_1}{k_2}(1 - e^{-k_2 t}) \qquad \text{(Eqn. 1.1)}$$

Where $C_s(t)$ is the concentration of the analyte in the sampler at time t, C_w is the concentration of the analyte in the aqueous environment and k_1 and k_2 are the upload and offload rate constants respectively. This equation can be further reduced down depending on the type of sampler being used, for example equilibrium or kinetic.

For *equilibrium passive samplers*, where the sampler exposure time is sufficiently long that equilibrium is established between the sampled and collected medium, Equation 1.1 reduces to

$$C_s = C_w \frac{k_1}{k_2} = C_w K \qquad \text{(Eqn.1.2)}$$

Where K is the phase water partition coefficient. When K is known it is possible to estimate the concentration of the dissolved analytes and as such determine the TWA for the water body in question (45).

The basic requirements of this equilibrium based approach are that stable concentrations are reached after a known response time, and that the sampler capacity is kept well below that of the sample concentration. This is to ensure that depletion can be avoided during extraction. If data on receiving phase-water partition coefficients is available this can allow for the calculation of the dissolved contaminant concentration. Equilibrium samplers are characterised by a rapid achievement of equilibrium between contaminants in the water to be sampled and contaminants inside the passive sampler (46).

For *kinetic passive samplers*, it is assumed that the rate of mass transfer between both mediums is linearly proportion to the difference in chemical activity of the analyte for both media. Equation 1.1 can then be reduced to

$$C_s(t) = C_w k_1 t \qquad \text{(Eqn. 1.3)}$$

This can in turn be rearranged to an equivalent relationship

$$M_s(t) = C_w R_s t \qquad \text{(Eqn 1.4)}$$

Where $M_s(t)$ is the mass of analyte accumulated in the receiving phase as exposure for length of time (t), R_s is the sampling rate which is the product of the first order rate constant for uptake of pollutant (k_1) and the volume of water that gives the same chemical activity as the volume of the receiving phase.

A series of papers have been published using a solved form of the above equations for the calculation of diffusion coefficients of pollutants into polymeric materials (47) (48) (49). The equation (Equation 1.1) was also modified for use in ATR-FTIR through a combination of the original equation and the general expression for absorbance in ATR. This resulted in the following equation (48):

$$\frac{A_t}{A_{eq}} = 1 - \frac{8}{\pi d_p (1 - e^{-\frac{2L}{d_p}})} \sum_{n=0}^{\infty} \frac{e^g [f e^{-\frac{2L}{d_p}} + (-1)^n \left(\frac{2}{d_p}\right)]}{(2n+1)(\frac{4}{d_p^2} + f^2)} \qquad \text{(Eqn. 1.5)}$$

Where:

$$f = \frac{(2n+1)\pi}{2L}$$

$$g = \frac{-D(2n+1)^2 \pi^2 t}{4L^2}$$

Kinetic samplers can be characterized by a high capacity for the collection of target pollutants. This high capacity ensures that the analytes can be enriched continuously, throughout the sampling period, allowing the TWA over the entire sampling period to be obtained.

Most commercially available passive samplers are considered bi-phase passive samplers. Bi-phase samplers generally consist of a receiving phase, which is non-polar, separated from the aquatic environment by a diffusion limiting membrane. Bi-phase samplers are more commonly available commercially and include semi-permeable membrane devices (SPMDs). In single phase passive samplers, e.g. silicone rubber (PDMS), the polymeric material acts as both the receiving phase and the diffusion limiting step. Common features of single phase passive sampling devices are the ease of construction, low cost and in some cases, the possibility of repeated usage (50).

There are two main accumulation regimes within a passive sampler, equilibrium and kinetic, which can be distinguished within the sampler during deployment in the field. Using the concentration of analytes in the sampled media and receiving phase, analytes can diffuse until a state of equilibrium is reached. Once this state is reached no further enrichment will take place within the sampler. Therefore the capacity of the receiving phase for the analytes of interests is directly proportional with the time span required for equilibrium to be reached.

When the relationship between the sampling rate and the analyte concentration is determined and known, TWA'S can then be calculated. However, there are certain criteria that need to be filled to ensure accuracy. The receiving phase must act as a 'zero sink', i.e. even if the concentration of the analyte around the sampler should decrease towards zero, the phase must ensure that the analytes remain trapped. Secondly the sampling rate must remain constant throughout the exposure period.

In kinetic sampling, it is assumed that the rate of mass transfer to the receiving phase is linearly proportional to the difference in chemical activity of the contaminant between the water phase and the receiving phase. Once the proportionality constant or the sampling rate is known the TWA concentration of a pollutant in the water phase can be calculated. The advantage of passive sampling is that they sequester contaminants from episodic events that would often not be detected with grab sampling, and can also be used in situations where the water concentration varies over time.

In recent years there has been development of a range of integrative passive sampling devices. The most widely used samplers are the SPMDs (51) for hydrophobic organic pollutants and the diffusive gradients in thin films (DGTs) (52) for metals and inorganic ions. The SPMDs were investigated to look at the effect that deployment time had on the expected levels of contaminants. It was found that a deployment of 14-30 days was sufficient to sample quantifiable levels of most relevant pollutants (51).

There have been several novel passive sampling devices that are suitable for monitoring a range of non-polar and polar organic chemicals, e.g. pesticides, pharmaceutical drugs and other emerging pollutants, recently developed. Attempts have been made towards minimizing the design of the passive sampler, combined with solventless sampler processing (53). An example of miniaturization which leads to green chemistry is a silicone elastomer, which is one of the materials that are currently being tested for use in analytical extraction techniques and passive sampling devices (54). Fast methodologies are now being developed for the recovery of environmental contaminants, these techniques include pressurized liquid extraction, ASE, MAE or sonication (55) (56).

In order to predict TWA water concentrations of contaminants from levels that accumulate in passive samplers, extensive calibrations are needed in order to characterise the uptake of chemicals into the passive sampler (57). This rate of uptake of chemicals depends upon the chemicals physio-chemical properties, but also on the sampler design. The rate of uptake can also be influenced by environmental variables such as temperature, flow rate, turbulence and bio-fouling of the sampler surface.

Booij *et al.* (58) described a method of estimating the uptake kinetics in both laboratory and field situations by spiking the passive sampling devices prior to exposure with a number of ‘performance reference compounds’ (PRCs) that do not occur in the environment. The release rate of these compounds can be used as a measure of the exchange kinetics between the sampler and water.

Uptake rates of analytes can be determined in the laboratory under a series of known conditions e.g. temperature, flow velocity and the absence of bio-fouling. When samplers are deployed in the environment however these conditions are not encountered identically which will result in non-ideal uptake rates. Through use of PRCs it is possible to correct this non-ideality and as such they are now gaining importance within the field (59). It is however, important to ensure that the PRC has similar properties to the target analyte, e.g. diffusion coefficient in the boundary layer, and solubility in the polymer, to the target analytes. These PRCs should also not occur in the deployment region as this can offset results; ideally PRCs are chosen to be an isotopic analog of the analyte. PRCs are generally labelled or unlabelled analytically non-interfering organic compounds, that have moderate to relatively high fugacity, and are added to the sampler prior to deployment (60).

1.4.3 PASSIVE SAMPLING VS. ACTIVE SAMPLING

While there are disadvantages to passive sampling as an alternative technique to active sampling it is important to note that there are many advantages and passive sampling has the potential to become a reliable, robust and cost effective tool in the analyses of water bodies.

Until now, monitoring of water quality has been heavily reliant on the collection (at set intervals of time) of spot water samples (19) where extraction and laboratory based analysis would then be carried out for both organic and inorganic pollutants. Although this method is both well established and also validated to the point where it is accepted for regulatory and law enforcement purposes, this method is only valid when it provides an entirely representative status of the water quality at that particular sampling site.

Active sampling methods represent the more commonly used approach for the collection and extraction of pollutant residues in water (61). These methods are ones in which physical intervention or external energy input is required for sample collection. However, following on from research that has been carried out over the last two decades it was found that there are considerable limitations to be found with this spot sampling method in relation to determining the total pollutant concentrations. When spot sampling is carried out there are many factors that will not be accounted for. One of these factors is metal speciation which may be a crucial factor in metal toxicity to aquatic organisms.

Spot water sampling only provides a snap shot of the water status (62) at the exact time of the sampling and does not provide any information on the bioavailability of pollutants within the water (63) (64). While it would be possible to continually repeat the spot sampling at the site this would be very expensive due to the costs of both the transport and the analysis. If another sampling method was deployed instead of repeated spot sampling e.g. passive sampling, more useful data on the variability of contaminant concentrations or temporal changes in toxicity (65), could be obtained at a lower cost (66) (67) .

There are many advantages for using a passive sampler compared to other sampling techniques. In passive sampling according to Fick's first law of diffusion, the flow of analytes from the surrounding sample through to the inside of the trap within the sampler is free. This means that the major driving force and mechanism of separation is based on concentration differences between the aqueous environment and the sampler. Through use of passive sampling, no pumps (68) or external energy are needed and this can make the passive sampler less complicated to use than the active equivalent (7). The passive sampler can be left to work unattended (69) (70) and in comparison to live biota can avoid drawbacks related to migration or mortality.

With the use of passive sampling only one device is needed at any one location for the duration of the sampling period. When grab sampling is used the sample will only represent the conditions of the water at that specific time, i.e. a snapshot, so in order to obtain time-averaged information many samples would be needed.

Another advantage of passive sampling in comparison with active sampling is with average concentrations of pollutants in the environment. A large number of samples need to be collected from one location for the sampling duration with active sampling (7). Both a pump and flow meter will also be required as the volume or flowing rate of the sample needs to be monitored. This leads to the active sampling being both costly and time consuming. Another factor that can be aggravated by this is that the sampling region is able to be disturbed by the pump which can lead to unreliable and un-reproducible results. The pumping can also cause loss of volatile compounds within the sample (23).

However there are some disadvantages to passive sampling that need to be addressed. For example the use of passive sampling is unsuitable to monitor short-term variations in analyte concentration (71), and also has limits within compliance testing of the WFD EQSs, and MAC standards as these are set for total water concentrations, with the exception of metals, whereas water concentrations measured by passive samplers are given as dissolved water concentrations (7) (2). It should also be noted that performance of validation and quality control with passive sampling can be more difficult that for traditional grab sampling. Passive sampling can be sensitive to change in temperature, water movements (hydrodynamics), flow rates and bio-fouling (Section 1.4.5).

1.4.4 SAMPLING DEVICES

Passive Sampling techniques are characterized by simplicity with regard to the sampler's construction as well as its maintenance. Therefore they find ever increasing application in the field of environmental research and analytics. When choosing a passive sampling method, one should not forget that some passive samplers require the time-consuming calibration step before being used in the field, whereas for some samplers relevant data has previously been published. The equipment used at the passive sampling stage is relatively simple and small, which is very important since the sampling sites are often situated great distances from the laboratory.

An appropriate calibration method is required for the design and quantification of passive sampling devices (72). Passive sampling devices have been studied over a variety of different research areas and have been applied to screen studies and source identification, quantitative determination, mapping of pollutant concentrations, and water quality monitoring.

1.4.4.1 SEMI-PERMEABLE MEMBRANE DEVICES (SPMDS)

SPMDs were introduced by Huckings and co-workers (73) as a new method for monitoring of lipophilic contaminants, and now it has attained the greatest importance and widespread application. The polymer, often thought to be non-permeable, actually consists of transport corridors of less than 10Å in diameter (74). These pores allow for the selective diffusion of hydrophobic organic chemicals, which are then sequestered in the lipid phase.

SPMDs are designed to sample chemicals that are dissolved in surface water, and mimic the bio-concentration of organic contaminants into the fatty tissues of organisms. The SPMD enables concentration of trace organic contaminant mixtures for analysis, toxicity assessments, and toxicity identification evaluations. The SPMD samplers have also been noted for chemically sampling in both groundwater and air.

The SPMDs consists of a neutral, high molecular weight lipid (>600 Daltons) such as triolein, which is then encased in a thick walled (50-100 µm) flat polyethylene membrane tube (75). The non-porous membrane allows the non-polar chemicals to pass through to the lipids where the chemicals are concentrated. Large molecules (>600 Daltons) and materials such as particulate matter and micro-organisms are excluded. A standard SPMD is 2.5 cm wide by 91.4 cm long and contains 1 mL of triolein.

SPMDs can sample hydrophobic organic contaminants from water or air under nearly any environmental conditions. Chemicals sampled by SPMDs include hydrophobic, bio-available organic chemicals such as polychlorinated biphenyls (PCBs) (76), PAHs (77), organochlorine pesticides, dioxins and furans, selected organophosphate and pyrethroid pesticides, organotin compounds and many other non-polar chemicals.

1.4.4.2 POLAR ORGANIC CHEMICAL INTEGRATIVE SAMPLER (POCIS)

The Polar Organic Chemical Integrative Sampler (POCIS) is designed to sample water soluble (polar or hydrophilic) organic chemicals from aqueous environments (78). This device relies on the diffusion and sorption to accumulate a total mass of the analytes. The deployment period can range from weeks to a month, and the device has neither mechanical nor moving parts. The POCIS samples chemicals from the dissolved phase, and mimics the respiratory exposure of aquatic organisms. The POCIS provides a reproducible means for monitoring contaminant levels and also concentrates trace organic contaminants for toxicity assessments and toxicity identification evaluate (TIE) approaches.

The POCIS consists of a solid material (sorbent) contained between two micro-porous polyethersulfone membranes (21). The membranes allow water and dissolved chemicals to pass through to the sorbent where the chemicals are trapped. Larger materials such as sediment and particulate matter are excluded. The membrane resists bio-fouling which can significantly reduce the amount of the chemical sampled and affect predicted uptake rates. The POCIS disk is constructed of two 130 µm thick x 47 mm diameter hydrophilic polyethersulfone membranes (0.1 µm pore size). The membranes enclose a resin/adsorbent mix which serves as sequestering medium.

Two configurations of the POCIS are commonly used (79), each of them containing different sorbents. A pesticide configuration contains a mixture of three sorbent materials (80 mg of solute ENV$^+$ and 20 mg of Biobeads S-X3 with surface dispersed powdered Ambersorb 1500 carbon) and is used for most pesticides, natural and synthetic hormones, many wastewater related chemicals, and other water-soluble organic chemicals. The pharmaceutical configuration contains a single sorbent (100 mg of Oasis HLB resin alone) that is designed for sampling most pharmaceutical classes. It is common to deploy POCIS of several different configurations together to maximize the types of chemicals sampled.

The POCIS can sample polar organic contaminants from water under nearly any environmental conditions. The samplers have been used successfully in fresh (80), estuarine (81) and marine waters (82). Chemicals sampled by the POCIS can include complex mixture of pesticides (78), prescription and non prescription drugs, personal care and common consumer products, industrial and domestic-use materials and degradation products of these compounds (83).

1.4.4.3 PASSIVE IN-SITU CONCENTRATION EXTRACTION SAMPLER (PISCES)

The Passive In-Situ Concentration Extraction Sampler (PISCES) (84) is designed to sample non-polar or hydrophobic organic chemicals in surface water. This device relies of diffusion and sorption to accumulate a total mass of analytes.

PISCES are constructed to be lightweight, rugged, easy to deploy, reusable and to allow easy addition and retrieval of solvent. The devices consist of a metal (brass) body with a flange at one end to retain the membrane and a screw cap at the other end to allow addition and removal of solvent. The cap is fitted with a Polytetrafluoroethylene (PTFE) vent filter that keeps water out but allows gases to escape. There are two configurations of PISCES; one has a flange diameter of 7.6 cm, a membrane area of 21 cm^2 and holds 100 mL of solvent. The other has a flange of 10 cm diameter, a membrane area of 50 cm^2 and holds 200 mL of solvent. Both samplers are approximately 9.5 cm long. Both the caps and flanges are sealed with standard sized Viton® o-rings. Low density polyethylene (LDPE) membranes typically are 100 µm thick. Thinner membranes have been evaluated but they do not yield higher sampling rates, and they were found not to be as sturdy as the 100 µm membranes. The solvent is analyzed by conventional analytical methods. The membrane excludes ionic, high molecular weight natural organic matter, and particulates, thereby simplifying and in some cases eliminating the need for cleanup of samples before analysis.

PISCES have found applications in monitoring of spatial distribution and tracing pollution sources in surface water and effluent wastewater for the monitoring of PCBs and tracing point sources of pollution (21). Successful sampling has been shown of alkyl benzenes (85), chlorinated benzenes (85), nonylphenols, PCBs (86) and PAHs (7). PISCES only sample truly dissolved compounds. Compounds bound to particles, dissolved organic matter or micelles are not directly sampled.

1.4.4.4 CHEMCATCHER (PASSIVE SAMPLER USING EMPORE DISK)

The Chemcatcher passive sampler samples analytes with diffusion of target analytes through a membrane, followed by accumulation of these analytes in a sorbent receiving phase. The first publication of the Chemcatcher passive sampler was in 2000 (87) and was developed to measure TWA'S of a range of target analytes (including polar, non-polar and metals) in aquatic environments.

Chemcatcher uses a PTFE support device to protect a layer of membrane which covers a solid receiving phase (e.g. C_{18} Empore disk). The Chemcatcher passive sampling system uses a receiving phase base on a solid sorbent immobilised in a polymeric matrix in the form of a disk and this overcomes a number of problems associated with the use of liquid receiving phases. Not only is the system physically robust but because the receiving phase can be selected from a wide range of commercially available phases, there is potential for increasing the range of analytes sampled or for making the sampling system selective, below a selection of phases that can be used is detailed.

The Chemcatcher passive sampler allows both hydrophobic and hydrophilic compounds to be sampled when taking into account the appropriate receiving phases, in terms of Empore disks, for Solid Phase Extraction (SPE). The body of the device, which supports both the diffusion limiting membrane and solid receiving phase and seals them in place, is made from PTFE.

There are two main configurations of Chemcatcher on the market; organic and inorganic. While using the organic Chemcatcher both polar and non-polar organic analytes can be sampled, and this method has found application as an integrative sampler with a sampling period of 14 days to 1 month, as well as measurements of TWA's of analyte concentrations in the environment. After exposure and before analysis a simple solvent extraction is carried out.

The second configuration of Chemcatcher is the inorganic sampler. This comprises of an immobilised chelating acceptor resin on a PTFE base and uses a cellulose acetate membrane filter acting as a thin diffusion layer. This sampler has been used for in-situ metal speciation in natural waters for Cd, Cu, Ni, Pb and Zn (25). After exposure the sample is then prepared by acid extraction.

Some of the analytes that can be sampled are polar or non-polar organics, some persistent organic pollutants (POPs) (57), organochlorine pesticides (88), PCBs (89), and PAHs (90). Accumulation rates and selectivity are regulated by the choice of both the diffusion limiting membrane and the solid phase receiving material; both are supported and sealed in place by an inert plastic housing. There is calibration data available for many chemicals and it is also possible to predict this data based on a model produced by Vrana *et al.* (90). A non linear regression was performed for the Log of the sampling rate from a series of nine calibration experiments using a third order polynomial function of Log K_{ow}. The plot obtained showed good correlation for sampling rates of compounds with Log K_{ow} in the range from 3.7 to 6.8. Through use of a model such as this it is possible to calculate the sampling rate for a large variety of pollutants.

1.4.5 FACTORS INFLUENCING PASSIVE SAMPLER PERFORMANCE

A sufficiently high sampling rate is required for a good sampler performance. This is even more important in the case of sampling for non-polar compounds as their levels in the water can be very low (<1 ppb) (91). The uptake rates of target analytes can be affected by a series of factors including the design of the sampler, the physiochemical properties of the analyte, and also environmental conditions that are present during the course of sampling.

Water sampling rates of target analytes by passive samplers can be altered by a series of different environmental factors, including temperature, hydrodynamics, bio-fouling, and water flow. These environmental variables are defined in more detail below (Sections 1.4.5.1 – 1.4.5.4) in order to aid with the more accurate estimation of ambient chemical concentration data.

1.4.5.1 SAMPLER DESIGN

Single and bi- phase passive sampling devices have both been developed. The more common type, bi-phase e.g. SPMD, usually consist of both a receiving phase, with an affinity for organic analytes, that get separated from the aqueous environment using a diffusion limiting membrane. For single phase passive samples, e.g. PDMS, the polymeric material acts both as the receiving phase and the diffusion limiting layer will simply be the water boundary layer present on all aquatic passive samplers (92) (93).

In the absence of bio-fouling the rate-limiting step is the receiving phase (93), and may be controlled by diffusion across the diffusion limiting membrane, or by the water diffusive boundary at the membrane-water interface. When passive samplers are applied to aqueous environments, the thickness of the water boundary layer can vary from 1 mm to less than 1 µm for quiescent and turbulent conditions respectively (94).

1.4.5.2 TEMPERATURE

An increase in the temperature of the aquatic environment can increase the water solubility and in turn decrease the partitioning to particles (95). This can have a large effect on passive sampler performance as passive samplers measure the dissolved fraction of polar organic compounds. Not only will there be a seasonal variation in temperature, it can also vary from day to day depending on the environment.

When looking at bi-phase passive samplers it has been seen in the literature that the effect of temperature on the sampling rates can be described using an Arrhenius plot. For SPMDs this relationship has been shown for a temperature range of 18-24°C and also for Empore disks, using polysulfone or low density polyethylene membranes, over a range of 4-20°C (87). In relation to single phase passive samplers, Smedes (93) carried out work on enrichment of silicone rubber with PCBs, PAHs (96) and chlorobenzenes and it was found that a 30% decrease in sampling rate occurred with a 10°C increase in temperature. With an increase in temperature there will be an increase in rate of diffusion. This is due to the fact that molecular diffusion coefficients will increase with temperature, which in turn will increase sampling rates for diffusion samplers (5). However it is not as simple to predict the effect that a change of temperature will have on diffusion through the polymeric layer, since some properties, e.g. fluidity and viscosity, of the polymer can also change with temperature (97)

1.4.5.3 HYDRODYNAMICS

Water turbulence affects the thickness of the unstirred layer of water that forms as part of the diffusion – limiting barrier near the sampling surface. Due to the fact that mass-transfer resistance is directly proportional to boundary layer thickness, this shows that the sampling rates of the target analytes will vary with the hydrodynamics of the deployment use (98). A series of PAHs and pesticides (fluoranthene, anthracene, hexachlorobenzene, dieldrin etc) were studied using Chemcatcher within laboratory conditions. It was found that with the exception of lindane an increase in sampling rate was observed with increasing flow velocity (57).

Nyoni *et al.* (84) carried out a study to determine the effect of hydrodynamics on the uptake rates of triazine compounds using a selective membrane assisted passive sampler (MAPS). The sampling rates were analysed for stirred and unstirred tanks and it was seen that when more turbulent conditions were applied there was an increase in sampling rates. The sampling rates, for both conditions, were then correlated to the Log K_{ow} of the analytes. For the more polar compounds (atrazine and simazine), a large increase was not seen with an increase in water turbulencehowever, for the more non-polar compounds, Log $K_{ow} > 3$, an increase in turbulence showed an increase in sampling rate (99).

1.4.5.4 BIO-FOULING

Any unprotected surface which is submersed in an aqueous ecosystem will eventually become a substrate for bacteria, flora and fauna, which may ultimately form a bio-film (23). The composition and thickness of this bio-film can vary depending on the aquatic system it is subject to. Bio-fouling affects the overall resistance to mass transfer by increasing the barrier thickness, and blocking any water-filled pores in the diffusion limiting membrane. If the membrane is made of a degradable material it is possible that colonising organisms may damage the surface and impede the uptake of target analytes (100).

Significant differences in sampling rates have been noted on some passive samplers due to the occurrence of bio-fouling. Depending on the target analyte, different percentage reductions of sampling rates have been noted. Ellis *et al.* reported a reduction of 26.2-38.6% in the sampling rate of phenanthrene in fouled SPMDs in comparison to un-fouled after a deployment in the upper Mississippi River (101). Another study carried out by Richardson *et al.* (102) demonstrated that the uptake of selected organochlorine pesticides (aldrin, α-HCH and p, p’ DDT) was reduced to between 78.4 and 38.8% of the concentration found in un-fouled controls. In the same study a selection of PAHs were also looked at (Anthracene, Fluoranthene, and Benzo (a) pyrene). The study was conducted over a four week period in aerated outdoor tanks with flow through seawater (SWIRE Marine Laboratory, Hong Kong).

From these results, it can be seen that reduced effects of bio-fouling were noticed with hydrophilic compounds which fits in with theoretical considerations. Within the passive sampler the bio-film can be counted as an additional layer between the collecting medium and the receiving phase. Due to this the bio-film needs to be permeated before the uptake of the target analytes into the receiving phase can occur. Hydrophilic compounds should permeate through this bio-film at a greater rate as the bio-film layer can be modelled as a water layer with dispersed organic matter (93). Another explanation is that the bio-film may hinder the extraction of the analytes from the disks after exposure (103).

1.4.6 LATEST TRENDS IN PASSIVE SAMPLING

1.4.6.1 COMBINATION OF PASSIVE SAMPLING DEVICES

There is no single passive sampling device that allows for the sampling of the very broad spectrum of analytes. Up to this point passive samplers were dedicated for hydrophobic pollutants e.g. PAHs and PCBs, however, recently there has be an increase in monitoring of compounds with medium to high polarity e.g. polar pesticides, pharmaceuticals. There is a need for assessing a wide range of pollutants within the environment. Due to the characteristics of known samplers, e.g. affinity for polar or non-polar compounds, it has made it imperative to deploy a selection of different passive samplers. Passive integrative samplers designed for a broad array of environmental contaminants provide a base for a holistic approach to the assessment of anthropogenic stressors in aquatic systems. These integrative samplers include SPMD for hydrophobic contaminants and POCIS for hydrophilic contaminants.

Petty (104) used a selection of three passive sampling devices (SPMDs, POCIS and SLMDs) and deployed these at five sites throughout a constructed wetlands complex. Through use of this suite of samplers a greater Log K_{ow} range was covered (0-10). POCIS samplers would be used for the sampling of hydrophilic compounds (Log K_{ow} 0-3) (e.g. Ibuprofen and phenelzine etc.) whereas SPMDs have a larger range for hydrophobic compounds (Log K_{ow} 3-10) (e.g. dieldrin, Lindane, p,p'-DDT etc.)

1.4.6.2 USE OF PASSIVE SAMPLERS IN LIEU OF BIO-ORGANISMS FOR ANALYTE UPTAKE

One of the major advantages of passive samplers is that they can determine the bio-availability of chemicals in a similar manner to select organisms. They have potential as biological surrogates, and scientists have investigated their use in aquatic environments, for example, in areas where the environment has a high concentration of contaminates which would affect the lifetime of organisms such as shellfish (105). There have been extensive studies into the possibilities of SPMDs as surrogate for bivalves in assessing the bio-availability of POPs in an aquatic system (106) (107). It has also been reported by Richardson *et al.* that SPMDs have similar uptake and response times as mussels (75). Target compound concentrations were determined in triplicate using both SPMDs and blue mussels (*Mytilus Edulis*). The results were found to be very comparable with a relative standard deviation that was generally less than 5%. There have been other studies in which SPMDs are compared to green-lipped mussels (*Perna viridis*) for the uptake of PAHs (75), chlorinated pesticides, PCBs (75) and petroleum hydrocarbons (106). In most cases however, contaminant levels based on passive sampling (in particular SPMD) and living organisms have been found to be different (43) (108).

Passive sampling devices have been used to assess the availability of aged organic compounds in soils. Good correlations were observed between the uptake of DDT, lindane, heptachlor, aldrin, dieldrin, and endrin by earthworms and the quantity of chemicals sorbed by C_{18} passive sampling devices (109). As environmental conditions can affect chemical uptake by living organisms, there is a possibility of a disparity between the number and the relative amounts of analyte residues detected in passive samplers and the tissues of test animals. This shows that the results obtained from passive sampling techniques and living organisms can support and complement each other and therefore are valuable tools for estimating the fate and impact of environmental contaminants.

1.4.6.3 ACCURACY IN TWA CONCENTRATIONS

TWA concentrations can be obtained using traditional grab sampling methods through repeated samples being obtained. One issue with this method is that obtaining the series of samples can often be physically and logistically difficult. This method would also generate large volumes of samples, and due to this, would increase the cost required to analyse them (110). Another more cost-effective method of obtaining TWA concentrations is through the use of a passive sampler. It is essential for the quantifying of the contaminants found in the environment that precise calibration of passive sampling devices is carried out. For this to be done, knowledge of uptake kinetics of different compounds is required. One method of increasing the accuracy in TWA concentrations is through the use of PRC which were discussed above(Section 1.4.2).

1.5 CONCLUSIONS

Passive sampling is a technique that could find much use in the current monitoring system within Europe. It has advantages compared to the traditional approach of grab sampling, due to its low cost, non-usage of power sources and ability to determine TWA concentrations of pollutants in the sampled environment. While the accuracy of passive sampling has increased in recent years to where it can be considered being on par with traditional methods, it is important to note that there are more variables with passive sampling than with grab sampling. It is important to study various environmental conditions that can affect uptake rates of pollutants, and in turn affect TWA results. One way of combating this issue is through the integration of PRCs.

While passive sampling shows great promise for long term monitoring of pollutants, it should be noted that for shorter term variation it is not suitable. One other issue that should be taken into consideration prior to the deployment of passive samplers is the security of the deployment site to allow for the possibility of vandalism occurring at the expense of loss of data.

By using passive samplers, in particular for pesticides, a greater window of understanding can be compiled for the usage of pesticides within the environment. Currently pesticides are analysed once a year, which in the case of pesticides does not complete an accurate representation of contaminant levels, in part due to the fact that only pesticides are used at select times during the year, for example during growing season, or harvesting season. By being able to obtain a TWA of periods such as one month at a time, it will be possible to obtain a more comprehensive picture of the use of pesticides within Ireland.

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CHAPTER 2: DEVELOPMENT OF ANALYTICAL METHODS FOR TESTING PASSIVE SAMPLING MATERIAL PERFORMANCE

2.1 INTRODUCTION

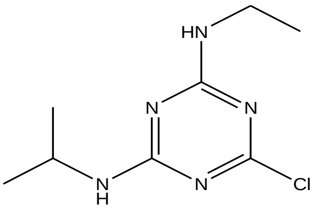
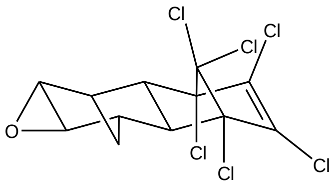
The monitoring of pesticide levels within the environment from a series of different matrices is very important for both human health and environmental control (1). One of the most important steps in the monitoring of pesticides is the pre-concentration and isolation of these analytes using various sample preparation techniques such as Solid Phase Extraction (SPE), Solid Phase Micro Extraction (SPME) and Supercritical Fluid Extraction (SFE). Pre-concentration can be an important step due to the low levels of analytes within environmental samples, typically in ngL^{-1} levels. Also with sample preparation, for example SPE, this can act not only to pre concentrate the sample, but can also 'clean-up' the sample matrix.

2.1.1 TARGET ANALYTES

Within Annex X of the WFD (2) 41 Priority Pollutants (PPs) are mentioned. These PPs have been broken down into four distinct groups; Pesticides, Volatile Organic Compounds (VOCs), Polycyclic Aromatic Hydrocarbons (PAHs) and Metals and Trace elements. Within this project the largest group, pesticides, was mainly concentrated on. Within the group of pesticides there is a large range of chemical and physical properties, e.g. molecular weight ranges from 201.66 to 406.93 $gmol^{-1}$ for simazine and DEHP respectively, and a range of Log K_{ow} of 2.61 to 6.36 for atrazine and p,p'-DDT.

In Table 2.1 below a more detailed overview of the two pesticides that were selected to represent the group of pesticides is shown. These two chemicals were selected due to being on different ends of the spectrum of the physical and chemical properties selected to be studied. The two pesticides, atrazine and dieldrin, were used as test analytes in the optimisation of methods and novel passive sampling materials.

Table 2.1: Selected physical and chemical properties of atrazine and dieldrin. (Log K_{ow}, M. Weight, M. Formula and structures)

	Atrazine	Dieldrin
Structure		
CAS Number	1912-24-9	60-57-1
M. Formula	$C_8H_{14}ClN_5$	$C_{12}H_8Cl_6O$
M. Weight ($gmol^{-1}$)	215.68	380.91
Log K_{ow}	2.34	5.4

Within the group of pesticides atrazine, is in the lower range of both molecular weight and Log K_{ow} (octanol-water partition ratio). The group of pesticides have a range of Log K_{ow} from 2.4 to 7.5 for simazine and DEHP respectively. A further reason that the above two chemicals were chosen to represent the group is due to their water solubility.

Atrazine is part of a class of herbicides which contain three heterocyclic nitrogen atoms in ring structures and are called triazines. Triazine herbicides inhibit photosynthesis. Atrazine is widely used on corn. Dieldrin is an insecticide used regularly from the 1950s to 1970 and was used as a pesticide for crops such as corn, citrus crops and cotton, also it was used to control locusts and mosquitoes, as a wood preserve and for termite control. Dieldrin is a non-polar compound and due to this will have a strong affinity for organic matter. It has a high potential for bioacculululation, indicated by a Log K_{ow} value between 4.3-6.2, and this can lead to bio concentration and bio magnify in living organisms.

2.1.2 SOLID PHASE EXTRACTION (SPE)

Solid Phase Extraction is a very popular sample preparation technique. Disposable cartridges were introduced for SPE in 1978 and in recent years much improvement has been seen in this technique, with the introduction of new sorbents and automation (3). SPE can be carried out both ‘off-line’ and ‘on-line’. The ‘on-line’ mode is directly connected to the system for analysis. These samples do not require further handing and due to this are very suitable for automated sampling. ‘On-line’ SPE has been hyphenated with both GC and LC, however due to the aqueous mobile phases commonly used for SPE. LC became the first robust on-line technique. Within this chapter work is carried out on ‘off line’ SPE.

On the market there are now many varieties of sorbent available; including non end-capped C18 silica’s and monofunctional silicas. These were developed to increase the number of non-modified silica groups at the surface to provide secondary polar interactions with solutes. Polymeric sorbents have also been introduced and have high specific areas in the range of 500—1200 m^2g^{-1} (4).

Solid Phase Extraction consists of four main steps which can be seen outlined below (Figure 2.1). Initially the sorbent is conditioned with a suitable solvent. This is carried out for two main reasons, improvement of the reproducibility of analyte retention and to reduce the carry through of sorbent impurities at the final elution step (5). Following on from this the sample is then loaded onto the cartridge, after which the cartridge is rinsed with a ‘weak’ solvent.

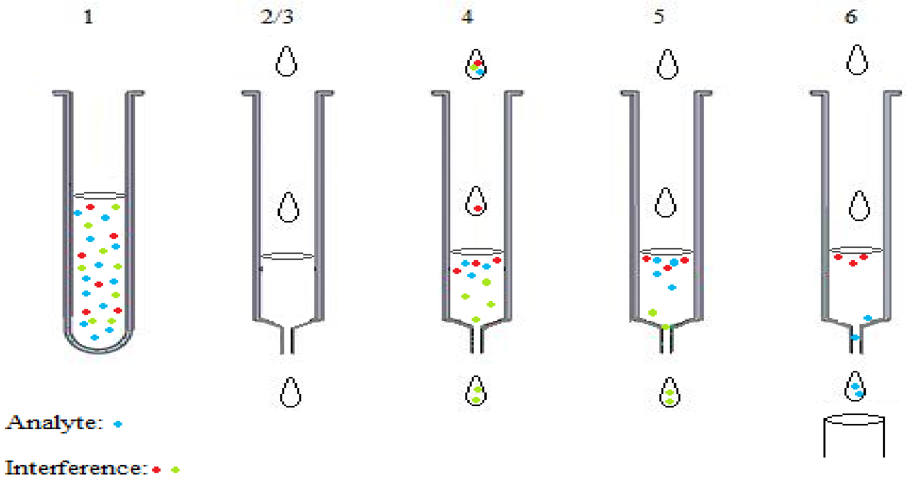


Figure 2.1: Schematic showing typical SPE steps 1: Sample with mixture of analyte and interferences.; 2/3: Conditioning steps; 4: Sample loading; 5: Washing and 6:Elution.

Once the cartridge has been rinsed it is generally dried under vacuum for a short period of time before elution with a water miscible organic solvent. By carrying out this drying step the volume of water retained by the eluting solvent is reduced.

Two of the most commonly used polymeric sorbents are Strata X and Oasis HLB, and there have been several comparisons of these two undertaken within the literature (6) (7) (8). While much work has been done using Oasis HLB for pesticides in the literature the results were comparable to those used with the Strata X cartridges. Within this chapter this Strata X cartridges were tested as a polymeric sorbent. Seven cartridges were tested two of which were polymeric with the other five being a selection of reverse phase cartridges. The two polymeric cartridges studied were Phenomenex Strata X (a chemically modified styrene divinylbenzene derivative) and Isolute ENV+ (a hydroxylated polystyrene divinylbenzene co polymer. D'Archivio *et al.*. (6) undertook a study comparing five SPE cartridges, Oasis HLB and Strata X included. During analysis one litre of groundwater was spiked with 2 or 5 μgL^{-1} and loaded onto the cartridges, eluted with methanol and acetonitrile (5 mL of each) and the samples were then analysed using HPLC. It was found that none of the cartridges were affected by pesticide concentration with the exception of Oasis HLB. The C18 sorbent tested was not able to retain all of the analytes tested, however Strata X and Oasis HLB was seen to. It could also be seen that as the spiked concentration increased the percentage recovery decreased slightly for Oasis HLB, 86-61% for simazine; whereas while testing the Strata X cartridge the recovery of simazine increased with an increase in spiked concentration (75-81%). While it appears that Oasis HLB cartridges are more commonly reported than Strata X within the literature, both of these polymeric sorbents show good extraction and recovery for pesticides.

2.1.3 GAS CHROMATOGRAPHY MASS SPECTROMETRY (GC-MS)

GC is an analytical technique that is used for the separation and analysis of compounds that can be vaporized without decomposition. GC is based on a solid stationary phase in which through physical absorption of analytes caused retention. In GC analysis the target analyte, in gaseous form, is transported through the column by the carrier gas(mobile phase). The mobile phases used in GC analysis are inert gases commonly helium, or unreactive gases such as nitrogen.

Gas Chromatography is one of the most commonly used methods for the determination of pesticides using a selection of detectors, Flame Photometric (FPD), Nitrogen-Phosphorus (NPD), Electron Capture Detectors (ECD) and Mass Spectrometers (MS). One issue that still occurs with pesticide analysis is the low abundance of residues; however through used of tandem MS/MS, Selected Ion Monitor (SIM) or Selected Reaction Monitor (SRM) the effects of the matrix can be reduced.

In the table below (Table 2.2) three published methods for GC analysis of pesticides are detailed. It can be seen that the same column make up (5% phenyl, 95% polydimethylsiloxane) is used. This is a non polar column, and was the column that was then selected for this projects GC analysis.

The methods mentioned below have been used for both pesticide and PAH analysis. Throughout this chapter it should be noted that the method developed on the GC-MS was for the identification and quantisation of pesticides only.

Table 2.2: Overview of select GC methods reported in the literature for the analysis of pesticides and priority pollutants mentioned in Annex X of the WFD

Authors	Method Description	Analytes mentioned in Annex X (WFD)
Pitarach *et al.*. (9)	*Column:* HP5-MS (30 m x 0.25 mm i.d., 0.25 µm). (5% phenyl, 95% polydimethylsiloxane) *Temperature Program:* 90°C (1 min); 20°Cmin^{-1} to 180°C; 3°C min^{-1} to 280°C; 30°Cmin^{-1} to 300°C (2.5 min). *EI Source temperature:* 250°C. *Flow rate:* 1 mLmin^{-1}. *Carrier gas:* Methane	Naphthalene, Pentachlorobenzene, 4-t-octylphenol, Trifluralin, Simazine, Atrazine, Anthracene, 4-n-Nonylphenol, Alachlor, Aldrin, Chlorpyrifos, Isodrin, Fluoranthene, Chlorfenvinphos, α & β Endosulfan, Dieldrin, p,p'-DDT, Indeno (1,2,3,cd)pyrene.
Pérez-Carrera *et al.*. (10)	*Column:* HP5-MS (30 m x 0.25 mm i.d., 0.25 µm). (5% phenyl, 95% polydimethylsiloxane) *Temperature Program:* 70°C (2 min); 30°Cmin^{-1} to 200°C (1 min); 3°C min^{-1} to 280°C (2 min). *EI Source temperature:* 250°C. *Flow rate:* 1 mLmin^{-1}. *Carrier gas:* Helium	Anthracene, Phenanthrene, Fluoranthene, Benzo [b] fluoranthene, Benzo [k] fluoranthene, Benzo [a] pyrene, Indeno [1,2,3-cd] anthracene, Benzo [ghi] perylene, Hexachlorobenzene, α & β endosulfan, Endrin, Dieldrin, Aldrin, 4,4'-DDT, Atrazine
Rissato *et al.*. (11)	*Column:* LM-5 (35 m x 0.25 mm i.d., 0.25 µm). (5% phenyl, 95% dimethylpolysiloxane) *Temperature Program:* 60°C; 25°Cmin^{-1} to 150°C (1 min); 3°C min^{-1} to 200°C (1 min); 8°Cmin^{-1} to 290°C (8 min). *EI Source temperature:* 250°C. *Flow rate:* 1 mLmin^{-1}. *Carrier gas:* Helium	Aldrin, α & β endosulfan, Hexachlorobenzene, Lindane, Alachlor, Atrazine, Simazine, Trifluralin, Chlorpyrifos

2.1.4 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

Liquid chromatography is a separation technique used in analytical chemistry to separate components using a liquid mobile phase. More commonly used is high performance liquid chromatography. In HPLC the sample is forced through the column (stationary phase) by a liquid at high pressure (mobile phase). HPLC can be separated into two sub categories based on the polarity of the mobile and stationary phases. These categories are normal phase and reverse phase chromatography. In the method where the stationary phase is more polar than the mobile phase e.g. silica stationary phase, hexane as the mobile phase, this is called normal phase liquid chromatography (NPLC). More commonly used in recent times is reversed phase liquid chromatography (RPLC), where the stationary phase is less polar than the mobile phase, e.g. C18 as the stationary phase, and a mixture of methanol and water for the mobile phase. In RPLC polar compounds are eluted first whilst non polar compounds are retained for longer.

LC is commonly used in the analysis of pesticides for cases of non-volatile, or thermally instable pesticides and their metabolites. When liquid chromatography is coupled with mass spectrometry (LC-MS) or with tandem mass spectrometry (LC-MS-MS) it can be a very powerful analytical technique for the identification and quantification of pesticide residues. While there is an increasing use of LC and LC-MS in the literature it should be noted that for the purpose of this project the LC method was used only as a short method for the screening of pesticides. In most studies only two analytes were present, atrazine and dieldrin. These were analysed on HPLC to test the optimisation of methods such as SPE (Section 2.2.2.1), and the optimisation of novel passive sampling materials (Chapter 3). The HPLC that was available for this analysis utilised an isocratic pump and as such analysis carried out was limited due to this.

Below (Table 2.3) four methods for the analysis of pesticides are detailed. One issue with HPLC methods for pesticides in the literature is the limitation of the isocratic pump mentioned above, however as this method was being developed to aid in the screening of novel passive sampling materials and not for the identification of pollutants from the environment a simpler method could be developed.

From looking at methods outlined in the literature it can be seen that the most commonly used column for analysis of pesticides is a C18, this is turn was selected for the HPLC analysis carried out throughout this project. Both acetonitrile: water and methanol:water mobile phases are commonly used for the analysis of pesticides. Acetonitrile:water was chosen for this project due to issues with sample make up in methanol for GC analysis which is outlined in more detail below (Section 2.3.2)

Table 2.3: Overview of select HPLC methods reported in the literature for the analysis of pesticides and priority pollutants mentioned in Annex X of the WFD.

Author	Method Description	Analytes mentioned in Annex X (WFD)
Melo *et al.*. (12)	*Mobile phase:* Acetonitrile: 0.01% aqueous NH4OH, pH 8.4 (35:65, v/v). *Flow rate* 0.7 mLmin^{-1}. *Detection:* UV (235 nm) *Column:* Purospher RP-18 5µm (125 mm x 4 mm i.d.)	Atrazine, simazine and diuron.
Ferrer *et al.*. (13)	*Mobile Phase:* ACN:Water (each containing 0.1% formic acid. Gradient (10% A (hold 5 min), linear gradient to 100% A after 30 min. *Flow rate:* 0.6 mLmin^{-1} *Detection:* Time of flight mass spectrometer *Column:* Zorbax Eclipse XDB-C8 5µm (150 mm x 4.6 mm i.d)	Alachlor, Atrazine, Chlorfenvinphos, Diuron, Isoproturon, Simazine and Trifluralin
Topuz *et al.*. (14)	*Mobile Phase:* Gradient profile of ACN:Water going from 50% ACN to 90% in 20 min, held for five min and then returned to initial conditions *Flow rate:* 1 mlmin^{-1} *Detection:* DAD set at 220 and 260 nm *Column:* C18, 5µM Luna Column (250 mm x 4.6 mm i.d.)	Trifluralin
Becouze *et al.*. (15)	*Mobile Phase:* 1 mM NH_4Ac in Milli-Q Water (A), Pure MeOH (B). 40% of B increased linearly to 100% in 33 min and held for 10 min. 15 min equilibration after each injection. Flow rate: 0.25 mLmin-1 Detection Mass spectrometer (3200 Q-Trap LC/MS/MS system) Column: C18 Isis Nucleodur EC 3 µm (125 mm x 2.1 mm)	Atrazine, diuron, isoproturon, simazine, chlorfenvinphos, octyl phenol, 4-nonyl phenol, fluoranthene, anthracene, benzo [b] fluoranthene, and benzo [k] fluoranthene

2.1.5 AIMS AND OBJECTIVES

The aim of this chapter is to develop and improve methods of extraction and analysis for priority pollutants in order to screen and optimise novel passive sampling materials. Analytical methods detailed within include Solid Phase Extraction (SPE) for sample preparation, High Performance Liquid Chromatography (HPLC), and Gas Chromatography Mass Spectrometry (GC-MS) for analysis.

2.2 MATERIALS AND METHODS

2.2.1 REAGENTS

Acetonitrile (HPLC grade), Methanol (HPLC grade), and pesticides were purchased from Sigma Aldrich (Tallaght Ireland) and were used without further processing. Strata X SPE cartridges were obtained from Phenomenex (Cheshire, England), all other SPE cartridges; Isolute C18, Isolute C18 (EC), Isolute MFC18, Isolute PH, Isolute ENV+, and Isolute C8 were obtained from (Biotage GB limited, United Kingdom)

2.2.2 INSTRUMENTATION

2.2.2.1 SOLID PHASE EXTRACTION (SPE)

For the SPE procedure Strata X 500 mg 6 mL cartridges were selected (detailed in Section 2.3.1). The cartridges were conditioned with 6 mL of methanol and 6 mL of ultra-pure water before extraction. The samples were loaded onto the cartridge. Following that a wash step was carried out to reduce surfactant remains with 6 ml of ultra-pure water. The retained analytes were eluted using 1 mL of acetonitrile and 1 mL of isopropyl alcohol. This 2 mL eluent was then dried under nitrogen and reconstituted with 1 mL of acetonitrile, and was ready for subsequent analysis.

2.2.2.2 GAS CHROMATOGRAPHY (GC)

2.2.2.2.1 INSTRUMENTATION

An HP 6890 series gas chromatograph connected to HP 5973 mass-selective detector equipped with Agilent 7683 auto sampler (Agilent technologies, USA) was used. The column used was a capillary column (D5-MS, 30 m × 0.25 mm i.d. ×0.25 μm, J&W Sci. USA)

2.1.2.2.2 SOLUTION PREPARATION

A stock standard solution of each of the pesticides was made up by weighing 10 mg of the individual pesticides, dissolving in acetonitrile and made up to 100 mL. These individual stock solutions were in turn used to make up a series of mixed standard solutions, whereby the concentration of mixed standard solutions is decided, depending upon sensitivity of each compound for the instrument and diluted down.

2.2.2.2.3 ANALYSIS

An HP 6890 series gas chromatograph connected to HP 5973 mass-selective detector was employed. The gas chromatograph was equipped with an Agilent 7683 auto sampler and split/splitless injector with electronic pressure control. A D5-MS, 30 m × 0.25 mm i.d. capillary column with a 0.25 µm film was used, with helium as carrier gas at a constant flow of 1.1 mL min^{-1}. The temperature programme was the following: initial temperature 40 °C, held for 2 min, 9 °C·min^{-1} ramp to 170 °C, 3 °C min^{-1} to 205 °C, then 1 °C min^{-1} to 208 °C finally by 20 °C min^{-1} to 290 °C and held for 13 min. The total analysis time was 36.42 min and the equilibration time 6 min. The temperature of the injection port was 250 °C and a 20 µL volume was injected in splitless mode. The development and validation of this method is detailed below (Section 2.3.2).

The mass spectrometer was operated in electron ionisation mode with an ionising energy of 70 eV, ion source temperature 230 °C, MS Quad temperature 150 °C, electron multiplier voltage (EMVolts) 1750 V when performing selected ion monitoring, scanning from m/z 50 to 400 at 3.25 s per scan; solvent delay, 8.5 min.

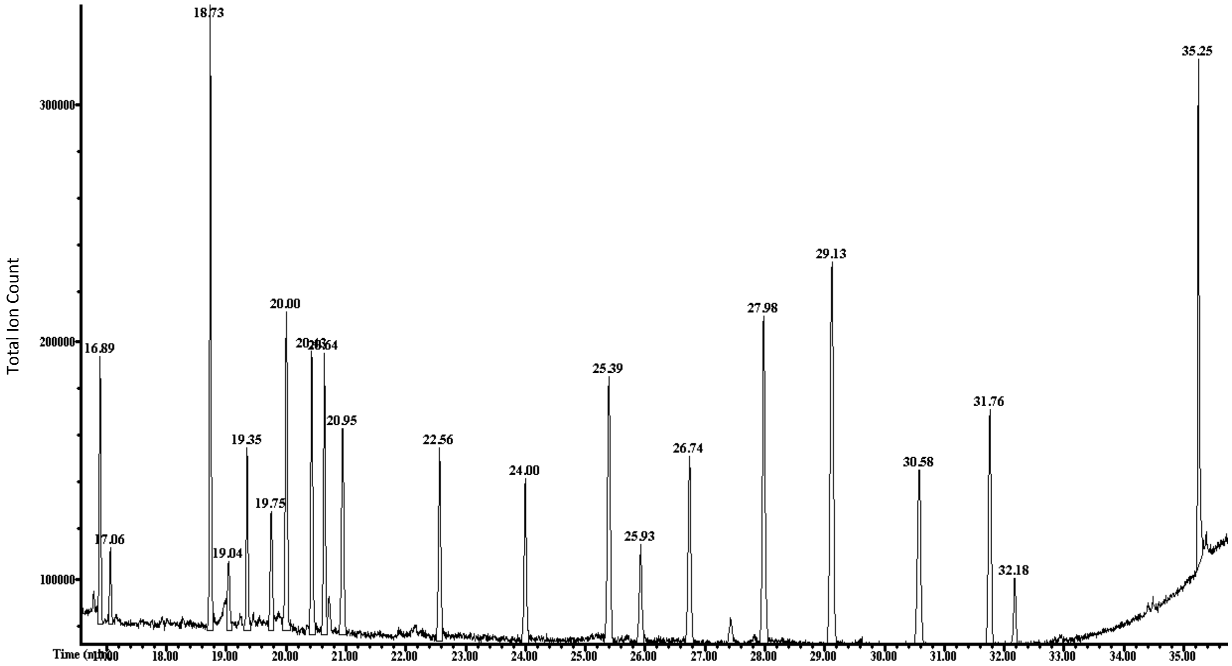


Figure 2.2: Chromatogram of the final method showing 18 pesticides. Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1}

to 290 °C (hold 2 min) .Peak Identification: haxachloro-1,3-butadiene 12.27 min, pentachlorobenzene 16.84 min, trifluralin 19.29 min, α lindane 19.95 min, hexachlorobenzene 20.00 min, simazine 20.37 min, atrazine 20.57 min, lindane 20.87, caffeine 22.49 min, alachlor 23.92 min, aldrin 25.31 min, chlorpyrifos 25.84 min, isodrin 26.65 min, chlorfenvinphos 27.90 min, endosulfan I 29.02 min, dieldrin 30.47 min, endrin 31.68 min, DEHP 35.21 min

2.2.2.3 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

2.2.2.3.1INSTRUMENTATION

Liquid chromatographic analysis was performed with a Agilent Technologies Liquid Chromatograph (Little Island, Cork Ireland), equipped with HPLC pump (Agilent 1100 series), auto sampler (Agilent 1100 series), VWD detector (Agilent 1200 series), injection valve (Injection volume: 20 µl). The separation was carried out using a C_{18}, 5 µm Luna column (250 mm × 4.6 mm ID, Phenomenex, CA, USA)

2.2.2.3.2 SOLUTION PREPARATION

A stock standard solution of each of the pesticides (atrazine and dieldrin) was made up by weighing 10 mg of the individual pesticides, dissolving in acetonitrile and made up to 100 mL. These individual stock solutions were in turn used to make up a series of mixed standard solutions, whereby the concentration of mixed standard solutions is decided, depending upon sensitivity of each compound for the instrument and diluted down.

2.2.2.3.1 ANALYSIS

The reverse phase separation was carried out using a C18 column and an isocratic binary mobile phase consisting of Acetonitrile:Water (95:10, v/v) pumped at a flow rate of 1 mL min^{-1}. Both solvents were filtered through a 0.45 µm x 47 mm nylon filter (Supelco, Bellefonte, PA, USA). Separation was made at room temperature. The total analysis time was 8 min. The development and validation of this method is detailed in below (Section 2.3.3)

2.3 RESULTS AND DISCUSSION

2.3.1 SOLID PHASE EXTRACTION

2.3.1.1 CARTRIDGE SELECTION

A series of SPE cartridges were selected to determine which showed the best extraction and percentage recovery of the pesticides selected for the study (Table 2.1). These cartridges with a variety of sorbents were investigated, both short and long chain, as well as polymeric to determine which sorbent showed the best affinity to the target analytes.

CARTRIDGE 1: ISOLUTE C18 (3 ML)

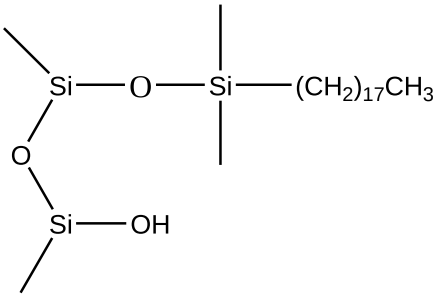


Figure 2.3: Chemical structure of Isolute C18, showing the silane group covalently bonded to the surface of a silica particle.

Isolute C18 is an octadecyl functionalized silica cartridge which is manufactured using trifunctional silane. This is an aqueous matrix and can be used for a wide polarity range of analytes. The primary retention mechanism is strongly non-polar, with a secondary mechanism whcih is polar and weak cation exchange (silanol interactions). The average particle size is 50 µm, with a nominal porosity 60 Å. These cartridges were used by D'Archivio *et al.* (6) in 2007 during a study which compared different sorbents for the extraction of pesticides. It was seen in this study that the Isolute C18 cartridges were not able to retain some of the pesticides (2, 4 D) and showed that this cartridge did not compare favourably with the other selected SPE sorbents. However when this cartridge was used for the extraction of alkylphenols and pesticides in human cord blood (16), results showed recoveries in the range of 65-120% with the exception of nonylphenol where the recoveries were above 200%. It can be argued that the C18 cartridge shows good extraction of pesticides with lower Log K_{ow}, but when less polar compounds were tested, 2,4 D and nonylphenol, issues arose.

CARTRIDGE 2: STRATA X (6 ML)

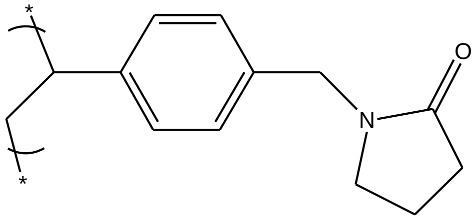


Figure 2.4: Chemical structure of Strata X showing polymeric sorbent

Strata X uses a polymeric sorbent which leads to reverse phase extraction. This can be used for both polar and non polar analytes. Strata-X cartridges are stable over 1-14 pH range. There are several types of bonding that can occur within this cartridge. Pi-Pi bonding can occur within the benzene ring, hydrogen bonding, Dipole-Dipole Interactions within the N-C=O region and also hydrophobic interactions within the benzene structure. These cartridges were used by D'Archivio *et al.* (6) in 2007 during a study which compared different sorbents for the extraction of pesticides, it was seen that Strata X retained all pesticides tested with results comparable only to Oasis HLB sorbents, showing better recovery of analytes in some cases (8) (7).

CARTRIDGE 3: ISOLUTE C18 (EC) (3 ML)

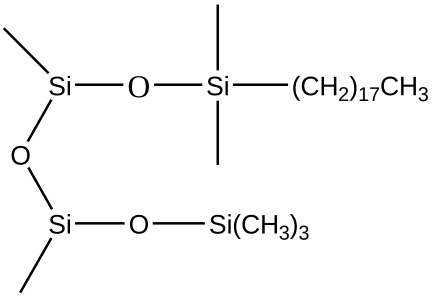


Figure 2.5: Chemical structure of Isolute C18 (EC), showing the silane and trimethyl silyl group covalently bonded to the surface of a silica particle.

Isolute C18 (EC) is an octadecyl endcapped functionalized silica cartridge which is manufactured using trifunctional silane. This is an aqueous matrix and can be used for a wide polarity range of analytes. The primary retention mechanism is non polar, due to the endcapped sorbent which is used to minimize secondary silanol interactions. The average particle size is 50 µm, with a nominal porosity 60 Å. Isolute C18 (EC) is the sorbent mentioned in US EPA method 525.2 for the analysis of PAHs and phthalates in waste and surface waters. (17)

CARTRIDGE 4: ISOLUTE MFC18 (1 ML)

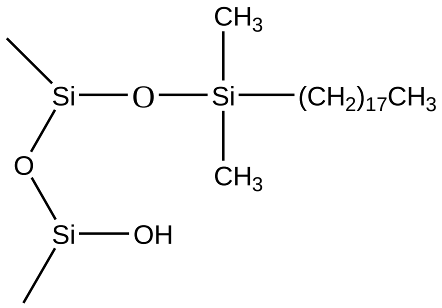


Figure 2.6: Chemical structure of Isolute MFC18, showing the monofunctional C18 silane covalently bonded to the surface of a silica particle.

Isolute MFC18 is an octadecyl (non endcapped) functionalized silica which is manufactured using monofunctional silica. It is a strong non-polar phase. The primary retention mechanisms are non-polar with a secondary mechanism of a polar and weak cation exchange. The average particle size is 50 µm, with a nominal porosity 125 Å.

CARTRIDGE 5: ISOLUTE PH

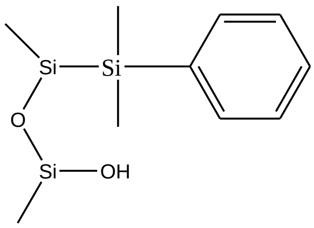


Figure 2.7: Chemical Structure of Isolute PH, showing the trifunctional silane covalently bonded to the surface of a silica particle.

Isolute PH is made of phenyl (non end capped) functionalized silica and manufactured using trifunctional silane. It has an average particle size of 50 µm, and a nominal porosity of 60 Å. It is a medium non-polar (hydrophobic) phase, and due to the fact that it uses non end capped silica there is additional silanol interactions noted.

CARTRIDGE 6: ISOLUTE ENV +

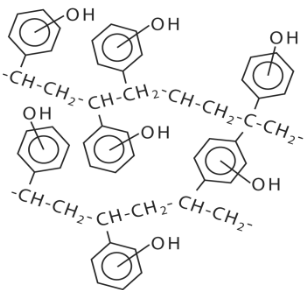


Figure 2.8: Chemical structure of Isolute ENV+ structure, showing a hydroxylated polystyrene divinyl benzene co-polymer

Isolute ENV+ is a hydroxylated polystyrene-divinylbenzene copolymer. This is a very strong non polar phase which is also water wettable. It is a cartridge that can be used for the extraction of very polar drugs and metabolites that would not be retained by a C8 or a C18 sorbent. It works on a non-polar retention mechanism. This sorbent has an average particle size of 90 µm and a nominal porosity of 800 Å. Isolute ENV+ cartridges were used in a study by Martinez *et al.* (18) which showed that the cartridges performaned well for the extraction of several pesticides, diuron and its by-products included. Another study was carried out by Fernandez-Alba *et al.* in 1998 (19) to monitor pesticides in groundwater. A large selection of insectides and fungicides were selected, including chlorfenvinphos and lindane, and all percentage recoveries were found to be 85% or over. The high percentage recoveries are due to the fact that the polymeric sorbents contain a lot of binding sites and also that they have high specific surface areas which can adsorb the target analytes.

CARTRIDGE 7: ISOLUTE C8

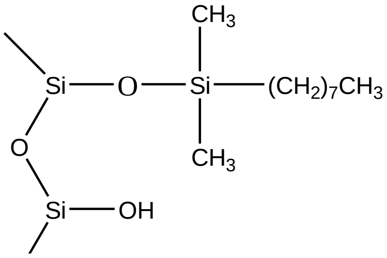


Figure 2.9: Chemical structure of Isolute C8, showing the silane group covalently bonded to the surface of a silica particle.

Isolute C8 is an octyl functionalized silica cartridge which is manufactured using monofunctional silane. This is an aqueous matrix and can be used for a wide polarity range of analytes. It is a medium non polar phase which is endcapped to provide additional silanol interactions which can be used in the analysis of a wide polarity range of analytes. The primary retention mechanism is strongly non-polar, with a secondary mechanism which is polar and weak cation exchange (silanol interactions). The average particle size is 50 µm, with a nominal porosity of 60 Å.

A schematic of the steps carried out for solid phase extraction has been shown above (Figure 2.1). The sample (step 1) contains a mixture of the target analytes and interferences within the matrix. The initial steps concentrating on the cartridge and sorbent (steps 2/3) are to condition the sorbent before a known quantity of sample is loaded (step 4) on to the cartridge. The target analytes will adsorb onto the selected sorbent and the interferences will be removed during the rinsing step (step 5). The sorbent is then dried under vacuum to ensure that none of the rinsing solvent remains present in the sorbent. The target analytes are then eluted (step 6) and the sample is now 'cleaned up' and can have a factor of pre concentration present. The factor of pre-concentration is dependent on both the loading volume (step 4) and elution volume step (step 6). A sample extraction method (20) based of a method outlined by Lacassie *et al.*. (Conditioning: 1 mL of methanol, 1 mL of water; Loading 1 mL, rinsing 2 mL DI H_2O, elution 2 mL ethyl acetate, evaporated and reconstituted with 100 µL of ethyl acetate) was chosen to aid in the determination of the optimum cartridge for the extraction of pesticides.

Table 2.4: Steps in the SPE process to determine the optimum SPE cartridge.

SPE Step	Chemicals used
Condition (step 2/3):	6 mL of methanol, 6 mL DI H_2O
Load (step 4):	1 mL of a 1 mgL^{-1} of target analytes
Wash (step 5):	6 mL DI H_2O
Elution (step 6):	1 mL Ethyl Acetate

The same procedure was carried out for all the cartridges mentioned above. An overview of results is seen below (Figure 2.10); each cartridge was analysed in triplicate. The percentage recovery was calculated for each cartridge using the following formula (Equation 2.1);

$$\frac{Concentration\ of\ analyte\ recovered}{Inital\ concentration\ of\ analyte} x \frac{100}{1} \qquad \text{(Eqn. 2.1)}$$

A selection of seven cartridges were tested to show the extraction and percentage recovery of both atrazine and dieldrin. The recovered samples were analysed using HPLC, with a mobile phase of 90:10 Acetonitrile: DI H_2O (detailed in section 2.3.3). For each sample the cartridge was prepared as mentioned above (Table 2.4), with methanol and water, each cartridge was loaded with 1 mgL^{-1} of target analytes, eluted and then run on HPLC.

It can be noted below that there is a significant difference in the percentage recoveries between the cartridges (5.46-63.03% for atrazine, 19.68-115.03% for dieldrin), with some cartridges showing very little percentage recovery (Isolute C18 (EC)), and others showing of preference of one analyte over the other (Isolute C18)

(Figure 2.10). The Isolute MFC18 showed the worst percentage recovery out of the seven cartridges tested (5.46% recovery of atrazine, and 20.98% for dieldrin). Strata X showed the best percentage recovery for both of the target analytes (63.03% for atrazine, 115.03% for dieldrin).

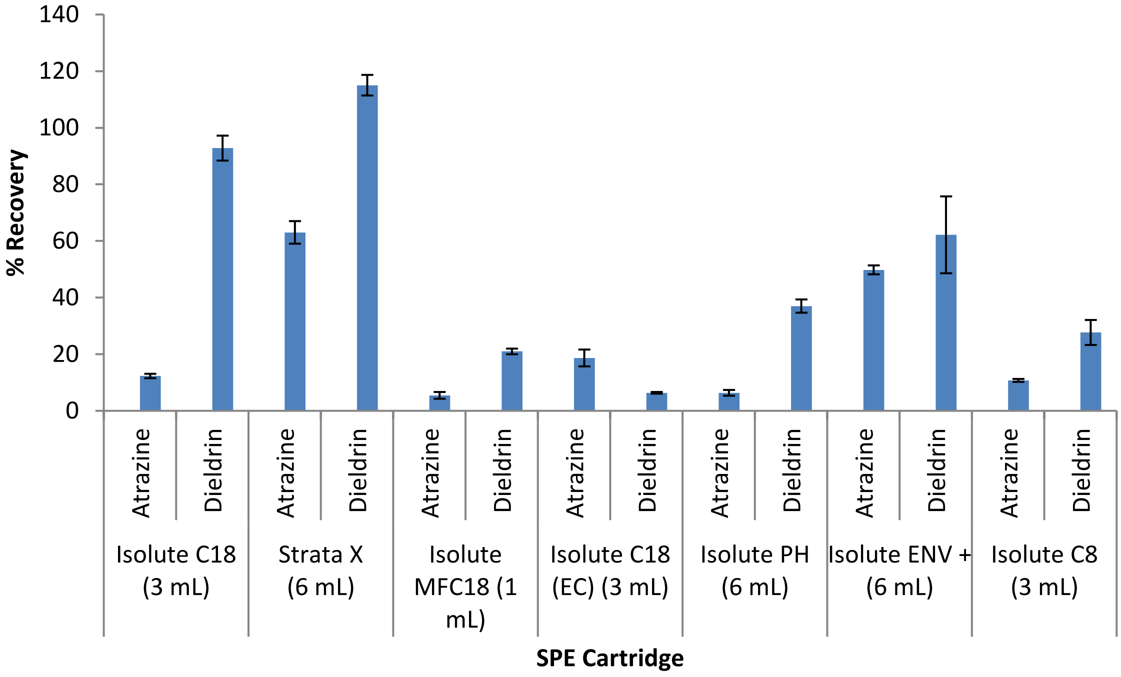


Figure 2.10: Overview of results for SPE Cartridge selection (n=3). Cartridges were conditioned with methanol and DI H_2O, Loaded with 1 mL of a 1 mgL^{-1} standard solution, rinsed with water and eluted with ethyl acetate before analysis using HPLC. The samples were analysed using a C18 (250 mm x 4.6 mm ID 5 µm Luna column, mobile phase 95:5 v/v acetonitrile:water.

Isolute C18 showed a good recovery for dieldrin (92.8%) but had a very low percentage recovery for atrazine (12.3%). One reason for this could come from looking at the polarities of the target analytes,dieldrin is strongly non polar whereas atrazine is a more polar compound. It is possible that while the dieldrin is adsorbed onto the sorbent that atrazine may have been absorbed onto the sorbent via the OH bond in the sorbent (Figure 2.3).

A trend can be seen between the Isolute C18, Isolute C18EC, and Isolute MFC18 cartridges. All of these sorbents have an octadecyl functionalised silica group within the sorbent as can be seen above (Figure 2.3, Figure 2.5, and Figure 2.6). In all cases dieldrin showed a greater percentage recovery than atrazine. When the sorbent was end-capped a dramatic decrease was noted in the percentage recovery of both target analytes, lending credence to the theory that the secondary mechanism of a polar and weak cation exchange was important in the retention of the analytes. However, it should be noted that while Isolute MFC18 has also this secondary mechanism it showed a large difference in the percentage recovery. This would lead one to believe that the mono-functional silica cannot compete in terms of percentage recovery of these target analytes in comparison to the tri-functional silane.

Two polymer cartridges were selected for this study, Strata X and Isolute ENV+. The Isolute ENV+ (Figure 2.8) shows a highly complex polymeric structure in contrast to the more basic structure of the Strata X polymer (Figure 2.4). Both polymers contain benzene rings which lend themselves to Pi-Pi bonding and also hydrophobic interactions. However, Strata X whilst having the benzene rings that are seen in Isolute ENV+ sorbents also has hydrogen bonding and dipole-dipole interactions occurring within the N-C=O region. Strata X is marketed as a sorbent for both polar and non polar compounds whereas Isolute ENV+ is targeted for very polar drugs and their metabolites. From this one would believe that the percentage recovery for atrazine should be favourable, which can be seen in the results above (Figure 2.10).

It was seen that the percentage recovery of atrazine (63.03% for Strata X) was greatest when using polymeric sorbents, with Strata X out performing Isolute ENV+ for both target analytes which can be accredited to the extra retention mechanism of the hydrogen bonding and dipole-dipole interactions occurring within the C-N=O region of the Strata X polymer.

Once the optimum cartridge had been selected (Strata X) a second study was undertaken to determine the solvent that would give the best recovery results.

2.3.1.2 ELUTION SOLVENT SELECTION

For this study the cartridge was Strata X as seen selected above (Section 2.3.1.1). A known volume (1 mL) of sample spiked with target analytes (1 mgL^{-1}) was loaded onto a conditioned cartridge and eluted with a range of different solvents to determine which solvent system showed the best recoveries. Five solvents were selected to determine which solvent system would give the optimum recovery results for atrazine and dieldrin.

Table 2.5: Steps in the SPE process to determine the optimum elution solvent.

SPE Step	Chemicals used
Condition (step 2/3):	6 mL of methanol, 6 mL DI H_2O
Load (step 4):	1 mL of a 1 mgL^{-1} of target analytes
Wash (step 5):	6 mL DI H_2O
Elution (step 6):	1 mL selection of solvents

Five different solvents were selected as possible eluent solvents for SPE. Selected physical and chemical properties of these solvents can be seen in the following table (Table 2.6)

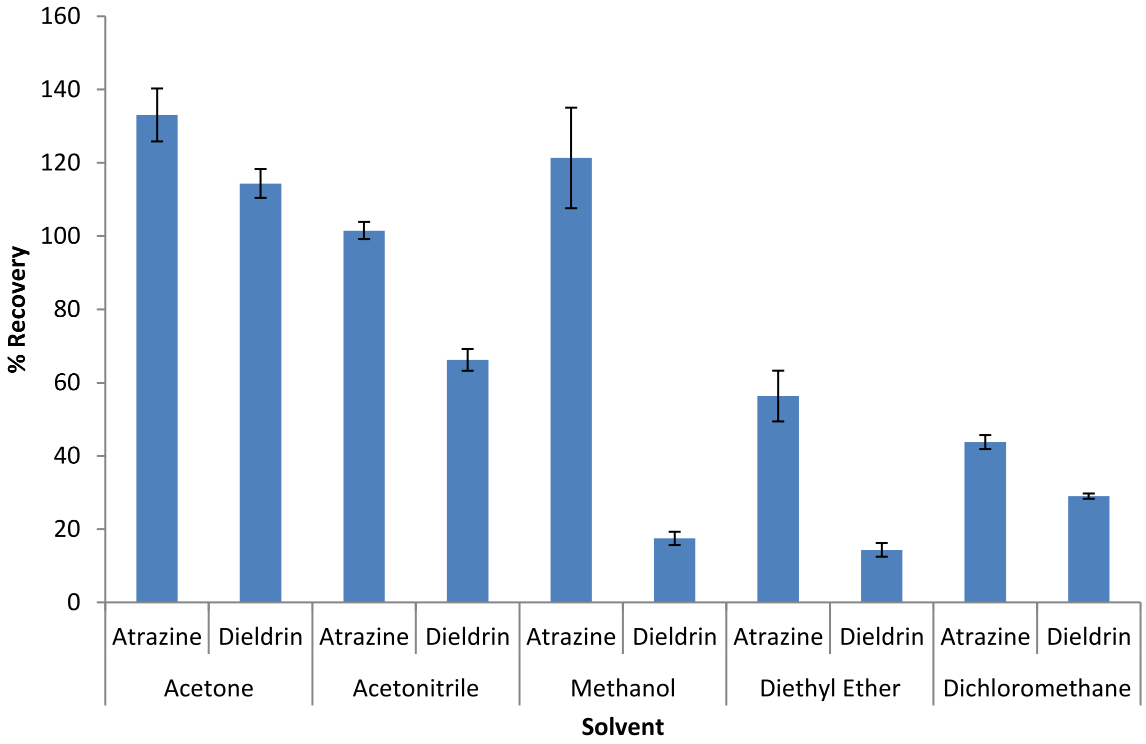


Figure 2.11: Results of elution solvents for optimum recovery of analytes (n=3). SPE was performed using Strata X (6 mL) cartridges. Cartridges were conditioned with methanol and DI H_2O, Loaded with 1 mL of a 1 mgL^{-1} standard solution, rinsed with water and eluted. The samples were analysed using a C18 (250 mm x 4.6 mm ID 5 µm Luna column, mobile phase 95:5 v/v acetonitrile:water.

It can be seen that while methanol showed a high percentage recovery of atrazine (121.3%), which would be expected due to the polarity of both the target analyte and solvent, it did not however, show a good percentage recovery of dieldrin (17.5%). This could be explained by looking also at the Snyder polarity index values for methanol (6.6) (Table 2.6). Of all the solvents tested for extraction of the analytes methanol had the highest index number. When acetone was used in place of ethyl acetate both of the percentage recoveries improved, to 133.07% and 114.35% for atrazine and dieldrin respectively. However, even with these high recoveries this solvent was not chosen for the final elution solvent as the percentage recoveries were too high to fit into the standards set by the EPA (70% - 130% (21)).

Diethyl ether gave a medium recovery for atrazine (56.34%) but a very low recovery for dieldrin (9.58%). Dichloromethane (DCM) gave a medium to low recovery for both compounds with 43.77% recovery obtained for atrazine, and 29.03% recovery for dieldrin. Using acetone and methanol, for both target analytes showed a percentage recovery of over 100%. This would show that not only that atrazine and dieldrin were extracted but also several contaminants.

Acetonitrile is a polar solvent, with a dipole moment of 3.84 D, Snyder index of 6.2 and is miscible with water. This was the solvent that was selected for further studies with recovery rates of 101.51% and 66.22% for atrazine and dieldrin respectively. However, the recovery of dieldrin is not as high as desired therefore it was decided to carry out further elution studies with the aim of optimization.

Table 2.6: Overview of average percentage recovery of target analytes using selected solvents. The samples were analysed using a C18 (250 mm x 4.6 mm ID 5 µm Luna column, mobile phase 95:5 v/v acetonitrile: DI water.

	Chemical Data			% Recovery	
Solvent	M.Weight (gmol^{-1})	Snyder Polarity Index	Log K_{ow}	*Atrazine*	*Dieldrin*
Methanol	32.04	6.6	-0.77	121.3	9.6
Acetonitrile	41.05	6.2	-0.34	101.5	66.2
Acetone	58.08	5.1	-0.24	133.1	114.4
Ethyl Acetate	88.11	4.3	0.73	63.03	115.03
DCM	84.93	3.4	1.25	43.8	29
Diethyl Ether	74.12	2.9	0.82	56.3	17.5

Snyder polarity index measures the intermolecular attraction between a solute and a solvent, which is a difference on the Hildebrand solubility parameter where this attraction is only measured for pure solvent. Snyder chose three chemicals to reflect the three forces which he had selected, ethanol to measure proton donation (acidity), diozane for proton acceptance and for measuring dipolar attraction nitro methane was selected.

The selected physical and chemical properties of the elution solvents tested are noted above (Table 2.6). These properties were tested against the percentage recoveries for both atrazine and dieldrin to determine if any correlation could be determined. However it was found that through plotting a series of graphs that no correlations were detected.

It should be noted that while ethyl acetate is mentioned above in the tabulated results (Table 2.6) it is not seen within the graphed results above (Figure 2.11). The results for ethyl acetate in the tabulated data are obtained from a previous study, the determination of optimum SPE cartridge (Section 2.3.1.1). A further study was carried out to determine if the addition of a second solvent in the extraction of the analytes would increase the percentage recovery of dieldrin.

2.3.1.3 OPTIMISATION OF ELUTION SOLVENT

For this study the SPE cartridge was Strata X (6 mL, 500 mg) and elution solvent was selected as acetonitrile (As selected in Section 2.3.1.1 and Section 2.3.1.2). However in aid to increase the percentage recovery of test analytes a secondary elution solvent was tested. A known volume (1 mL) of sample spiked with target analytes was loaded onto a conditioned cartridge (6 mL methanol, 6 mL DI Water) and eluted 1 mL of acetonitrile followed by 1 mL of a varied selection of different solvents to determine which solvent system showed the best recoveries. Five solvents were selected to determine which solvent system would give the optimum recovery results as can be seen below (Table 2.78).

Table 2.7: Steps in the SPE process to determine the optimum secondary elution solvent

SPE Step	Chemicals used
Condition (step 2/3):	6 mL of methanol, 6 mL DI H_2O
Load (step 4):	1 mL of a 1 mgL^{-1} of target analytes
Wash (step 5):	6 mL DI H_2O
Elution (step 6):	1 mL Acetonitrile
	1 mL Varied solvent

As the elution volume has now increased to 2 mL the eleunt once collected was evaporated under nitrogen and reconstituted to 1 mL using acetonitrile before analysis was carried out.

For all of the solvents, with the exception of toluene, the percentage recovery of dieldrin increased. Of the four solvents tested two, toluene and chloroform, had recoveries that exceeded the EPA limits. Of the remaining solvents IPA was chosen over DCM due to the percentage recoveries of atrazine decreasing through use of DCM. This can be explained due to volatility of the solvent and the solubility of atrazine within.

Table 2.8: Recoveries for secondary solvent elution for atrazine and dieldrin. The SPE process was carried out with Strata X cartridges, conditioning 6 mL methanol, 6 mL DI H_2O, elution with 1 mL of acetonitrile followed by 1 mL of IPA. The samples were analysed using a C18 (250 mm x 4.6 mm ID 5 µm Luna column, mobile phase 95:5 v/v acetonitrile: DI water.

	% Recoveries	
	Atrazine	**Dieldrin**
Toluene	145.51	60.25
Chloroform	108.06	133.05
Isopropanol	104.6	110.35
DCM	76.46	106.24

2.3.1.4 BREAKTHROUGH STUDIES

While the percentage recovery, defined above (Equation 2.1), is the ratio between amount extracted and amount applied to the cartridge the breakthrough volume represents the maximum sample volume or concentration that can be applied with a theoretical 100% recovery. In general there are two common causes of breakthrough, the retention capacity of the sorbent bed is overloaded due to a high concentration of either analyte or sorbed matrix components or that the sorbent bed may fail to adequately retain the analytes due to the provision of an insufficient number of theoretical plates for retention volumes to be independent of the plate count (5).

2.3.1.4.1 BREAKTHROUGH VOLUME ANALYSIS

The breakthrough volume for a target analyte and SPE sorbent can be determined by studying its breakthrough curve. For the initial sampling phase the analytes are quantitatively retained by the sorbent up the point where the sample volume exceeds the retention capacity of the sorbent. When further volumes of sample are passed through the sorbent bed the analytes are not quantitatively retained, and this will then reach a point where the concentration of the analyte entering the sorbent is equal to the concentration exiting. Six different volumes spiked with the target analytes were loaded onto the Strata X cartridges and the results are shown below (Table 2.9).

Table 2.9: Results from the breakthrough volume study for atrazine and dieldrin (n=3). . The SPE process was carried out with Strata X cartridges, conditioning 6 mL methanol, 6 mL DI H_2O, elution with 1 mL of acetonitrile followed by 1 mL of IPA. The samples were analysed using a C18 (250 mm x 4.6 mm ID 5 µm Luna column, mobile phase 95:5 v/v acetonitrile:DI water.

Sample Volume (mL)	% Recoveries	
	Atrazine	**Dieldrin**
1	100	100
250	122.20	80.86
500	104.74	75.52
750	32.68	18.95
1000	17.56	15.30
2000	10.80	16.89

The concentration of the target analytes was compared to the value obtained through loading with 1 mL of spiked sample. As can be seen from the results the concentration of the analytes fell within limits set by the US EPA at volumes up to 500 mL (Table 2.9). After this volume the concentrations of analytes detected decreased. From looking at the chromatograms obtained after analysis of the 'wash' step, an increase in the concentration of both target analytes could be observed (up to 65.23% and 78.89% for atrazine and dieldrin respectively) which showed the breakthrough of analytes.

2.3.1.4.2 BREAKTHROUGH CONCENTRATION ANALYSIS

The capacity of a SPE column depends on both the stationary phase and the bed volume of the sorbent. Several columns containing 200 mg of sorbent were found to adsorb up to 3-12 mg of analyte without breakthrough. One factor to consider in this however is the concentrations of analytes that would be found in the environment where concentrations are at ngL^{-1} to mgL^{-1} levels, due to this breakthrough should not typically occur due to overloading of the SPE column.

The breakthrough concentration was carried out at seven different concentration levels ranging from 1 – 50 mgL^{-1}.

Table 2.10: Results from the concentration breakthrough study for target analytes. . The SPE process was carried out with Strata X cartridges, conditioning 6 mL methanol, 6 mL DI H_2O, elution with 1 mL of acetonitrile followed by 1 mL of IPA. The samples were analysed using a C18 (250 mm x 4.6 mm ID 5 µm Luna column, mobile phase 95:5 v/v acetonitrile: DI water.

	% Recoveries	
Concentration mgL^{-1}	Atrazine	Dieldrin
1	121.29	105.59
5	91.32	109.25
10	73.04	108.27
20	78.27	107.72
30	68.33	73.51
40	61.45	42.25
50	63.58	30.17

2.3.5 SPE OF PESTICIDE STANDARD

During the development of the GC-MS method for analysis of pesticides an internal standard was used (Section 2.3.2). The internal standard chosen for the method was caffeine. An internal standard is a compound that is purposely added to both the samples and standards at a known concentration in order to provide a basis for comparison in quantisation. This method can improve precision when the main sources of error are related to sample preparation or injection due to the fact that these errors will affect both the internal standard and the analyte peak in the same manner.

Following the optimisation of the SPE method a standard stock solution (1 mgL^{-1}; 500 mL) was loaded onto a conditioned Strata X cartridge and SPE was carried out as detailed above (Section 2.3.1.3). The eluent was then analysed using a developed GC-MS method, which is seen below (Figure 2.15) and outlined in section 2.3.2.4

It can be seen that all percentage recoveries were below 100% which is in accordance to EPA standards (Table 2.11). Three compounds were found to have percentage recoveries below 40%; pentachlorobenzene, hexachlorobenzene and simazine. Both pentachlorobenzene and hexachlorobenzene are considered to be semi volatile which would explain their low percentage recoveries, as a high percentage could have evaporated off during the evaporation prior to reconstitution with acetonitrile.

Table 2.11: Percentage Recoveries of pesticides following SPE. SPE was carried out with Strata X cartridge (6 mL, 500 mg) with the following method; Conditioning 6 mL methanol, 6 mL DI H_2O; Rinsing 6 mL DI H2O; Elution 1 mL acetonitrile, 1 mL isopropyl alcohol, evaporated down and reconstituted with 1 mL of acetonitrile. Samples were analysed using GC-MS. (Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min))

CAS Number	Compound	% Recovery
608-93-5	Pentachlorobenzene	15.33
1582-09-8	Trifluralin	74.04
118-74-1	Hexachlorobenzene	33.78
122-34-9	Simazine	34.36
1912-24-9	Atrazine	84.38
58-89-9	Lindane	76.85
15972-60-8	Alachlor	65.30
309-00-2	Aldrin	69.66
2921-88-2	Chlorpyrifos	91.92
465-73-6	Isodrin	64.89
470-90-6	Clofenvinfos	68.11
959-98-8	Endosulfan I	88.27
56816-04-7	Dieldrin	93.37
72-20-8	Endrin	90.73
117-81-7	DEHP	91.86

2.3.2 GAS CHROMATOGRAPHY – MASS SPECTROMETRY

2.3.2.1 INSTRUMENTATION

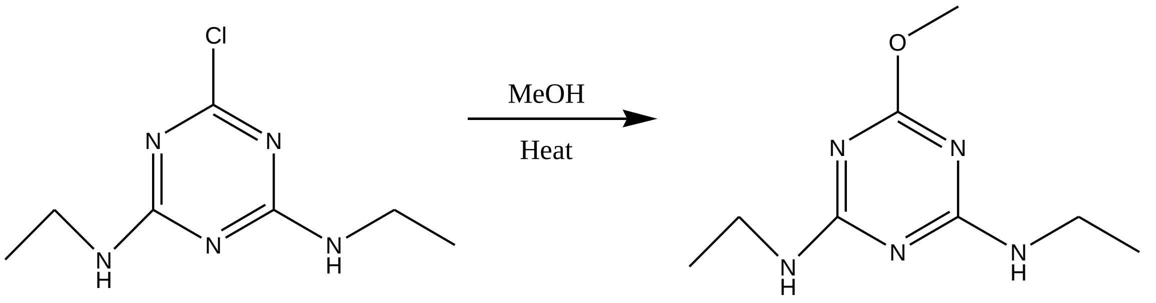
A HP 6890 series gas chromatograph connected to HP 5973 mass-selective detector equipped with an Agilent 7683 auto sampler (Agilent technologies, USA) was used for GC analysis. The column used was a capillary column (HP5-MS, 30 m x 0.25 mm i.d. x 0.25 µm, Agilent Technologies, Palo Alto, CA, USA).

Data was analysed using both WD Search 32 and MSD ChemStation (Agilent) both of which were equipped with NIST98 data base for the identification of peaks.

The samples were initially ran using the following method; 80°C (hold 1 min), 30°Cmin^{-1} to 180°C, 3°Cmin^{-1} to 205°C (hold 4 min), 20°C min^{-1} to 290°C.

2.3.2.2 SOLUTION PREPARATION

Initially all samples were made up using methanol. However, from looking at the mass spectrums of all analytes it was seen that simazine did not have the expected mass spectrum. it was noted that the base peak was 197, this would have been impossible if the peak was simazine as it has a molecular weight of 201, and the loss of a molecular mass of m/z 4 would be highly unusual.



6-chloro-N^2,N^4-diethyl-1,3,5-triazine-2,4-diamine

Simazine
m/z 201

N^2,N^4-diethyl-6-methoxy-1,3,5-triazine-2,4-diamine
Simatone
m/z 197

Figure 2.12: Proposed structure for analyte formed when sample of simazine was made up in methanol and analysed using GC-MS.

This peak that was identified is proposed as N^2,N^4 diethyl-6-methoxy-1,3,5-triazine-2,4-diamine, also known as Simatone (Figure 2.13). When looking at the mass spectrum below (Figure 2.13) it can be seen that the base peak is m/z 197 which is the molecular weight of simatone, which is 4 a.m.u less than simazine. The peak at m/z 182 can be attributed to the loss of a methyl group (m/z 15). When a C_2H_5 (m/z 28) group is cleaved off the molecule a peaks at m/z 169, when both of the ethyl groups are cleaved we can see a peak at m/z 139.

It can be seen when looking at the mass spectra of both simatone (Figure 2.13) and simazine (Figure 2.14), that they are both quite similar in respect to the lower masses. This can be explained by the fact the only difference in the structure is a methoxy group in place of a chlorine atom on simatone in comparison to simazine. On the s-triazine ring there are three branches is both cases and only one of these in different. On both mass spectra peaks at m/z 28 and m/z 44 are seen which can be attributed to the cleavage of an ethyl group and a C_2H_6N group respectively.

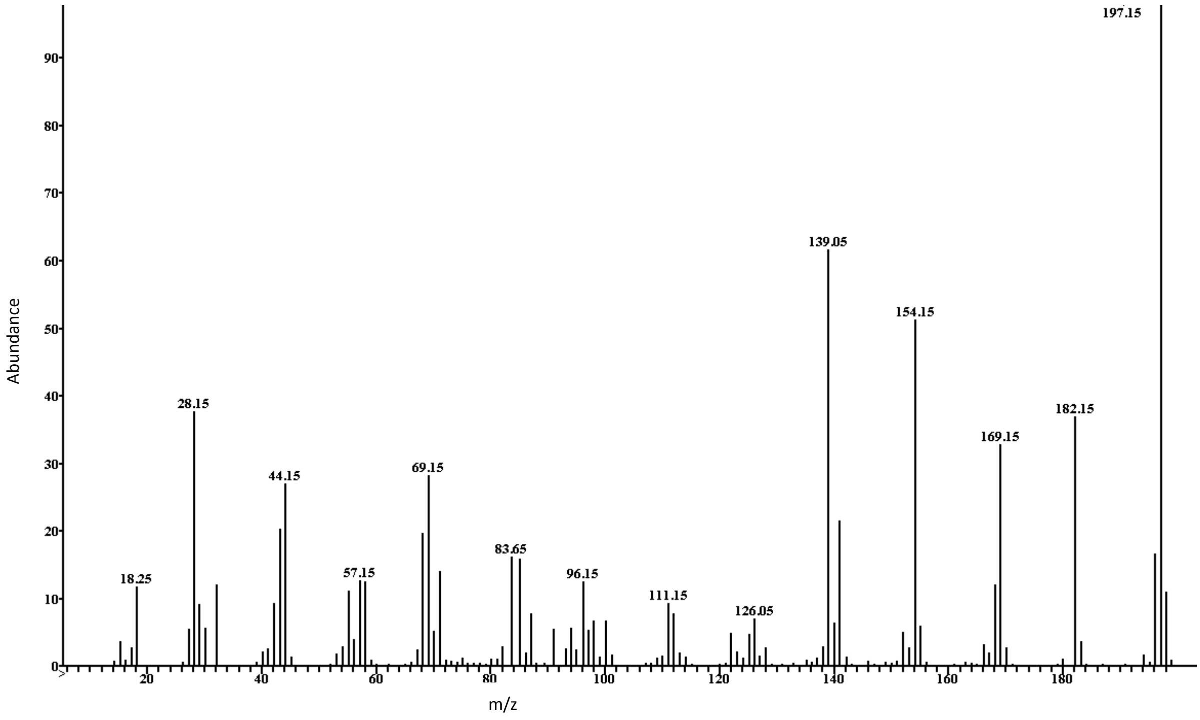


Figure 2.13: Mass spectrum of Simatone in methanol, analysed on a HP-5MS, temperature programme (80°C (hold 1 min), 30°Cmin^{-1} to 180°C, 3°Cmin^{-1} to 205°C (hold 4 min), 20°C min^{-1} to 290°C).

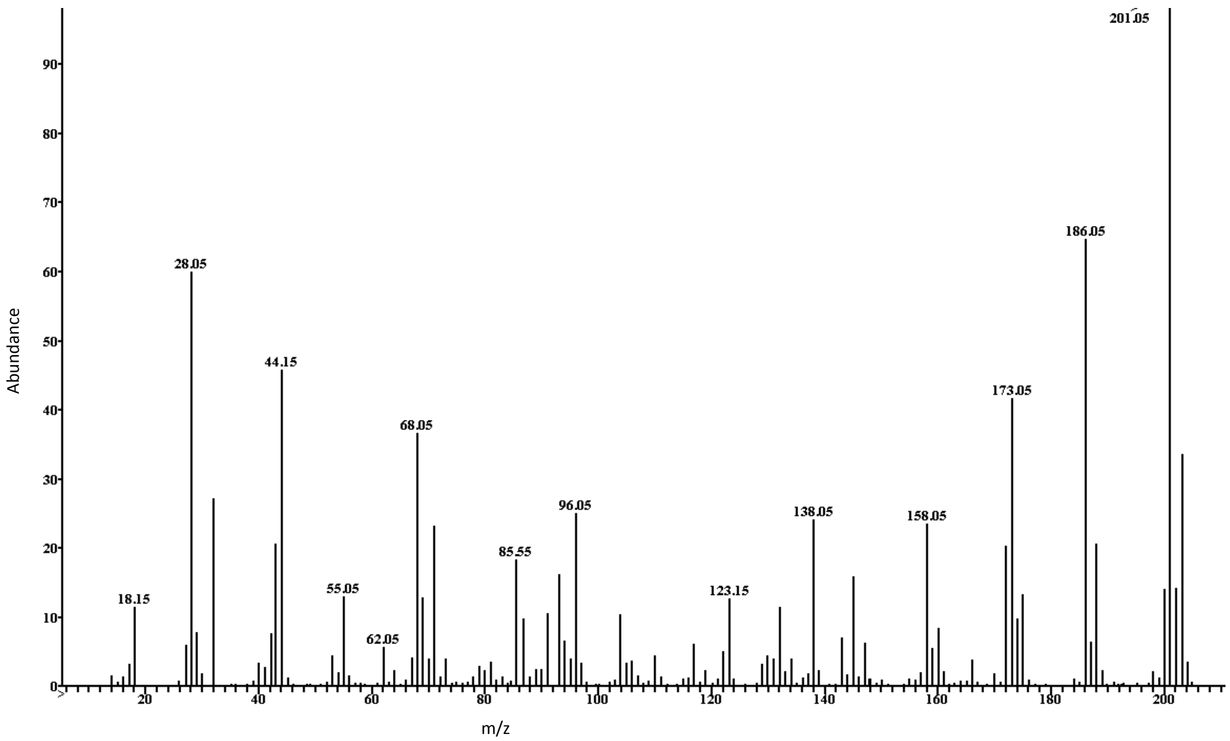


Figure 2.14: Mass spectrum of simazine in acetonitrile, analysed on a HP-5MS, temperature programme (80°C (hold 1 min), 30°C min^{-1} to 180°C, 3°C min^{-1} to 205°C (hold 4 min), 20°C min^{-1} to 290°C)

There are however, some differences between the two spectra. It can be seen (Figure 2.14) that when the simazine standard was made up in acetonitrile in place of methanol that the base peak was m/z 201. This is what is expected from simazine which has a molecular weight of 201 $gmol^{-1}$. A peak at m/z 186 shows the loss of m/z 15 which can be related to the cleavage of a methyl group. The peak at m/z 173 shows a loss of m/z 28 the same mass as an ethyl group.

After this was discovered it was noted that the solvent for the samples needed to be changed. It has been previously shown that acetonitrile could be used to dissolved pesticides. All pesticides were made up at a concentration of 0.01 gL^{-1}, and injected into the method previously developed on the GC (Section 2.3.2.3). This method needed to be adapted further for optimum separation of the compounds, and this optimization is detailed below (Section 2.3.2.2 and Section 2.3.2.3). In each case the graphs and tables will only indicate the compounds that at any stage in the optimization were found to have a resolution below 1.5.

Resolution was calculated using the following formula:

$$R = \frac{2(T_2 - T_1)}{(W_1 + W_2)} \quad \text{(Eqn. 2.2)}$$

Where T_1 and T_2 refer to the retention time of the two peaks, and W_1 and W_2 to the width of peaks in minutes.

2.3.2.3 INITIAL METHOD DEVELOPMENT

The temperature programme for the initial method was adapted from the previous GC method in which methanol was used as a solvent (Figure 2.3.2.1). The method was as follows; initial temperature 80°C (hold 3 min), 30 °Cmin^{-1} to 180 °C, 3 °C min^{-1} to 205 °C (hold 4 min), 20 °Cmin^{-1} to 290 °C (hold 2 min). A stock standard of 18 pesticides and caffeine (used as internal standard) was injected. When looking at the resulting chromatogram it was noted that there were five peaks that were below a resolution of 1.5. In order to optimise the separation of all of the peaks included in the table below several paramaters were modified with the optimum results being selected (Table 2.12). These parameters are detailed below in the following sections. Within the following sections a series of tables will be shown outlining only the peaks that had a resolution below 1.5

2.3.2.3.1 INITIAL HOLD TIME

In varience of the initial hold time there was 8 compounds with a resolution below 1.5 in one of the five different cases. For ease of viewing the table below shows five compounds that had a resolution of below 1.5 in all cases, as the other three mentioned only showed poor resolution in one out of five cases.

Table 2.12: Resolution of peaks at varying initial hold times. (Temp programme: initial temperature 40°C (hold varied min), 10 °Cmin^{-1} to 180 °C, 3 °C min^{-1} to 205 °C (hold 4 min), 20 °Cmin^{-1} to 290 °C (hold 2 min).

	Initial Hold Time (min)				
Analyte	2	3	4	5	6
Pentachlorobenzene-trifluralin	0.835	1.074	1.005	0.788	0.408
Hexachlorobenzene (HCB)-simazine	1.090	1.235	1.385	1.209	1.110
Atrazine –α Lindane	0.983	0.806	0.936	0.990	0.924
α Lindane – Hexachlorobenzene	0.898	0.878	0.892	0.815	0.882
Lindane – Caffeine	1.115	0.651	1.044	1.212	1.188

For ease of viewing in the above table some of the compounds have been omitted at there was in some cases only one hold time where there resolution was below the requisite 1.5 (e.g. alachlor-aldrin and dieldrin-endrin at hold time 4 min).

While looking at the results in the table above (Table 2.12) it can be seen that a hold time of 4 minutes appears to give the best results. However as mentioned above, when the hold time was increased to four minutes this affected the resolution of peaks that eluted at later times than those shown above(Table 2.12). For this reason the optimum hold time selected to continue on was 2 min. Including this optimisation the method that was selected to continue with the optimisation was; initial temperature 40°C (hold 2 min), 10 °Cmin^{-1} to 180 °C, 3 °C min^{-1} to 205 °C (hold 4 min), 20 °Cmin^{-1} to 290 °C (hold 2 min)

2.3.2.3.2. SECOND TEMPERATURE

The next factor that was optimized was the second temperature within the program and this was varied upwards from 160°C, in the table the resolution of the compounds at the different temperatures are outlined (Table 2.13 The optimum temperature that was chosen was 170°C

When looking at the analytes noted below (Table 2.13) it can be seen that there are three peaks in common with the optimisation of initial hold time (Table 2.12) that continue to have resolutions of below 1.5, however three new 'problem peaks' have also been identified. In the case of Isodrin-clorfenviphos the resolution falls below 1.5 at both 160°C and 190°C.

Table 2.13: Resolution of peaks at varying secondary temperatures (Temp programme: initial temperature 40°C (hold 2 min), 10 °Cmin^{-1} to varied °C, 3 °C min^{-1} to 205 °C (hold 4 min), 20 °Cmin^{-1} to 290 °C (hold 2 min)

	Temperature			
Compound	**160 °C**	**170 °C**	**180 °C**	**190 °C**
Pentachlorobenzene-trifluralin	0.795	0.803	0.835	0.797
HCB-Simazine	1.351	1.381	1.090	1.165
Atrazine-α Lindane	0.705	0.561	0.983	0.624
Isodrin-Chlorfenvinphos	0.080	3.348	3.520	1.336
Chlorfenvinphos-Endosulfan I	0.205	0.971	0.789	1.829
Endosulfan II- DEHP	1.309	1.393	1.219	1.084

It can be seen above (Table 2.13) that the initial method with a temperature of 160°C showed poor resolution of peaks. It also should be noted that with the exception of isodrin, the altering of the second temperature did not noticeably increase the resolution of peaks. While the resolution of isodrin-chlorfenvinphos was greatest using 180°C as the second temperature within the programme, several of the other problem analytes (HCB-Simazine, chlorfenvinphos-Endosulfan I, Endosulfan II-DEHP) showed better resolution at 170°C which was then selected to continue. The method programme was now as follows; initial temperature 40°C (hold 2 min), 10 °Cmin^{-1} to 170 °C, 3 °C min^{-1} to 205 °C (hold 4 min), 20 °Cmin^{-1} to 290 °C (hold 2 min)

2.3.2.3.3 SECOND TEMPERATURE RAMP

A series of temperature ramps were tested to determine the optimum separation conditions of the 18 pesticides and the internal standard. The second temperature ramp was varied from 1-5 °Cmin^{-1} (initially had been 3 °Cmin^{-1}). From looking at the resolution values that were obtained below (Table 2.14) it can be seen that with the exception of HCB-Simazine and Simazine-Atrazine, that the resolution of peaks were not above the desired value of 1.5. However it should also be noted that from this it was possible to study the behaviour of different analytes within the matrix as the variables were altered. Nevertheless, the changing of these conditions did not lead to an optimised resolution of peaks within the method method and so knowledge was taken from this and the behaviour of the analytes to increase and decreases in temperature to aid in the development of a temperature program which is outlined in the sections below (Section 2.3.2.4).

Table 2.14: Overview of resolution of peaks over varying temperature ramps Temp programme: initial temperature 40°C (hold 2 min), 10 ^{o}Cmin^{-1} to 170 ^{o}C, varied ^{o}C min^{-1} to 205 ^{o}C (hold 4 min), 20 ^{o}Cmin^{-1} to 290 ^{o}C (hold 2 min)

	Ramp ^{o}Cmin^{-1}				
	1	2	3	4	5
Pentachlorobenzene-trifluralin	0.622	0.810	0.803	0.803	0.634
HCB-Simazine	1.385	1.771	0.381	1.820	1.249
Simazine-Atrazine	2.398	2.325	0.671	2.293	1.901
Atrazine- α Lindane	0.718	0.513	0.561	0.574	0.577
α Lindane -Hexachlorobenzene	0.727	0.173	0.839	0.902	0.966
Lindane - Caffeine	0.952	0.211	0.935	0.959	0.850
Chlorfenvinphos- Endosulfan I	1.095	0.143	0.971	0.889	0.795
Endosulfan II -DEHP	0.137	0.972	1.393	1.158	1.005

2.3.2.4 SECOND TEST METHOD

The second method was chosen based on the performance of the compounds at different temperatures and settings from what can be seen above (Section 2.3.3). This method was developed by looking at the best resolution of the problem peaks and at which temperatures/times that they appeared (Section 2.3.2.3). The method was as follows; initial temperature 40°C (hold 2 min), 9 $^oCmin^{-1}$ to 170 °C, 4.5 $^oCmin^{-1}$ to 205 °C, 1 $^oCmin^{-1}$ to 208 °C, 20 $^oCmin^{-1}$ to 290 °C (hold 2 min). While this was injected one further optimization of the method was carried out. The second ramp (initially 4.5 $^oCmin^{-1}$) was varied and the results can be seen below (Table 2.15). It can immediately be seen that this temperature program had less problem peaks than previous methods trialed with only three of the problem peaks having resolutions above 1.5. The optimum temperature ramp from this optimisation was found to be 3 $^oCmin^{-1}$.

Table 2.15: Resolution for compounds over a range of temperature ramps (Initial temperature 40°C (hold 2 min), 9 $^oCmin^{-1}$ to 170 °C, varied $^oCmin^{-1}$ to 205 °C, 1$^oCmin^{-1}$ to 208 °C, 20 $^oCmin^{-1}$ to 290 °C (hold 2 min)

	Second Ramp ($^oCmin^{-1}$)				
Compound	2	2.5	3	4.5	5.5
α lindane-HCB	2.106	1.762	1.877	1.142	0.944
HCB-Simazine	1.276	1.002	1.363	0.890	0.875
Simazine-Atrazine	2.176	2.135	2.363	1.272	1.853
Atrazine-Lindane	0.782	0.734	0.823	0.432	0.574
Lindane-Caffeine	1.210	1.154	1.458	1.082	1.173
Endosulfan II-DEHP	2.399	2.328	2.061	1.038	0.959

A standard of concentration 0.02 mgL^{-1} of a pesticide mix was injected and below i retention times and resolution values of all peaks can be seen outlined (Table 2.16).

Table 2.16: Full list of pesticides, retention time and resolution during final method. (Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min)

Target Analyte	R. Time (min)	Width (min)	Resolution
Pentachlorobenzene	16.89	0.111	4.45
Trifluralin	19.35	0.124	2.50
α Lindane	19.75	0.228	2.28
Hexachlorobenzene	**20.00**	**0.15**	**1.33**
Simazine	20.43	0.172	2.65
Atrazine	**20.64**	**0.137**	**1.37**
Lindane	20.95	0.173	1.95
Caffeine	22.57	0.219	8.28
Alachlor	23.99	0.146	7.85
Aldrin	25.39	0.149	9.47
Chlorpyrifos	25.93	0.181	3.22
Isodrin	26.74	0.245	3.83
Chlorfenvinphos	27.99	0.22	5.34
Endosulfan I	29.13	0.243	4.93
Dieldrin	30.58	0.199	6.60
Endrin	31.77	0.329	4.47
Endosulfan II	32.18	0.139	1.78
DEHP	35.25	0.22	17.10

As can be seen above only two compounds, hexachlorobenzene and atrazine do not have a resolution greater then 1.5 (Table 2.16), however due to the amount of compounds in the mixture and the closeness of these two values to 1.5 on TIC, this is acceptable. All peaks were identified both by injecting standard solutions of the target analytes, and also from mass spectrums obtained using the NIST98 database.

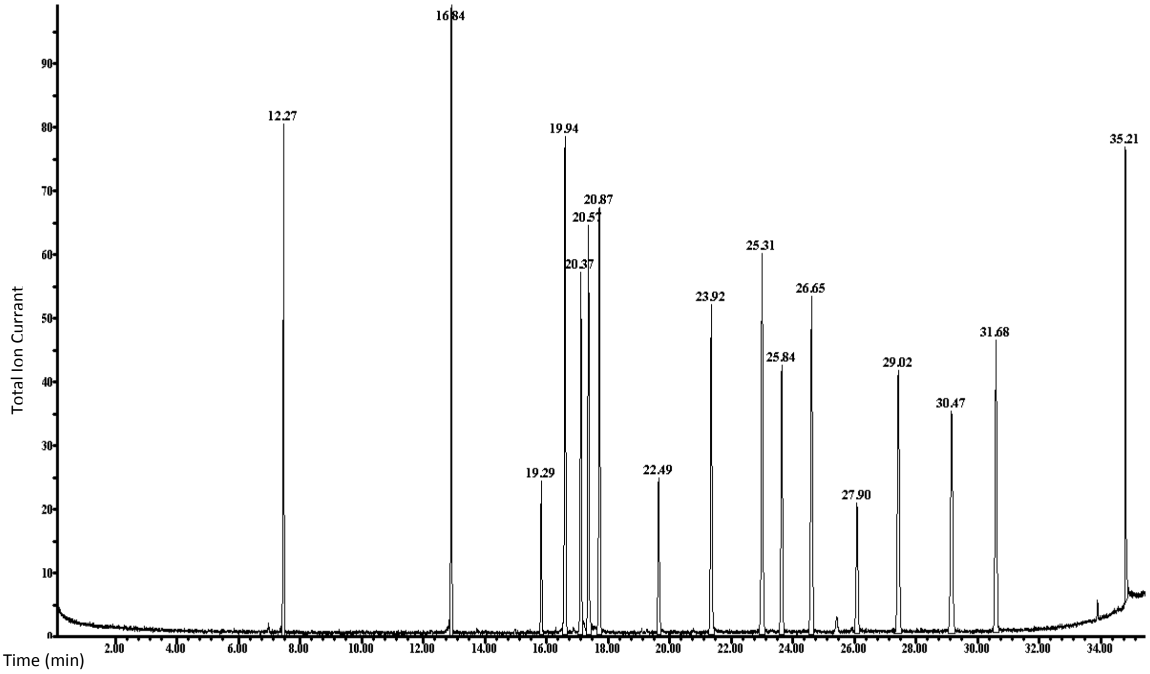


Figure 2.15: Chromatogram of the final method showing 18 pesticides. Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min) .Peak Identification: haxachloro-1,3-butadiene 12.27 min, pentachlorobenzene 16.84 min, trifluralin 19.29 min, α lindane 19.95 min, hexachlorobenzene 20.00 min, simazine 20.37 min, atrazine 20.57 min, lindane 20.87, caffeine 22.49 min, alachlor 23.92 min, aldrin 25.31 min, chlorpyrifos 25.84 min, isodrin 26.65 min, chlorfenvinphos 27.90 min, endosulfan I 29.02 min, dieldrin 30.47 min, endrin 31.68 min, DEHP 35.21 min

2.3.2.5 METHOD VALIDATION

2.3.2.5.1 PRECISION

The precision of any analytical procedure expresses the closeness of agreement between a series of measurements. Precision may be considered at three different levels; repeatability, intermediate precision and reproducibility. Repeatability expresses the precision under the same operation conditions over a short interval of time. Intermediate precision expresses the variations within a lab e.g. different days, different analysts ordifferent equipment. Reproducibility expresses the precision between laboratories.

The precision of this analytical method was measured in two ways; repeatability and intermediate precision. For intermediate precision the sample was made up and injected by two different people. Intermediate precision of the GC-MS itself was not carried out as a second GC-MS was not available. Reproducibility measurements were also not carried out for the same reason. The precision of an analytical procedure is usually expressed as the variance or standard deviation of a series of measurements.

To test the accuracy and repeatability of the method the same sample was injected six times and the retention times and area counts were compared for each of the compounds.

Once the six injections were completed the averages and standard deviations were obtained for both the retention time data and also for the area counts. From this it was possible to determine the percentage relative standard deviation of the area counts, which is the value for the average area count of the compound divided by the standard deviation calculated and then this value is multiplied by one hundred.

Relative standard deviation was calculated using the following formula (22)

$$\%RSDRSD = \frac{StandarStandard\ Deviationd\ de\ viation}{MeanMean} x\ \frac{100}{1}\ x$$

(Eqn. 2.3)

A good relative standard deviation is considered to be below five percent. As can be seen in the table below that all of the relative standard deviations obtained fell below the five percent mark with the highest relative standard deviation for the area counts obtained being 4.585 and the lowest value obtained was 2.560 (Table 2.17). The retention time data had much lower values as the retention times were found to be very repeatable. All of these relative standard deviation values were below 0.013%.

Table 2.17: Repeatability results for GC-MS method (n=8). Injection of a 1 mgL^{-1} sample six times. (Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min))

	Retention time			Area Counts		
Compound	**Average**	**Std Dev**	**%RSD**	**Average**	**Std Dev**	**%RSD**
Hexachloro-1,3-Butadiene	12.267	0.001	0.011	5380525	149869	2.785
Pentachlorobenzene	16.839	0.001	0.003	7563351	267518	3.537
Trifluralin	19.288	0.002	0.013	2727440	123111	4.514
Hexachlorobenzene	19.934	0.002	0.009	7507018	235610	3.139
Simazine	20.367	0.002	0.008	4704643	192662	4.095
Atrazine	20.574	0.002	0.011	5555765	210991	3.798
Lindane	20.871	0.001	0.006	7082966	204833	2.892
Caffeine	22.491	0.002	0.008	6275436	182053	2.901
Alachlor	23.920	0.002	0.008	6185289	275012	4.446
Aldrin	25.305	0.003	0.012	6938721	179921	2.593
Chlorpyrifos	25.839	0.002	0.007	4337785	198893	4.585
Isodrin	26.653	0.003	0.011	6502144	166470	2.560
Clofenvinfos	27.894	0.003	0.009	2597216	75051	2.890
Endosulfan I	29.017	0.002	0.006	5735189	173790	3.030
Dieldrin	30.467	0.004	0.013	5453512	208731	3.828
Endrin	31.678	0.003	0.010	5815796	193027	3.319
DEHP	35.213	0.002	0.005	5049870	182082	3.606

Following on from the reproducibility test, intermediate precision was carried out. Intermediate precision looks at the variance when the same sample is analysed using two distinct instruments, lab personal or analysis on different days. For this intermediate precision a second researcher aided in the analysis of a stock sample using the same GC-MS and analytical method.

Table 2.18: Results obtained for intermediate precision. A 1 mgL^{-1} stock solution was injected by a second analyst to show intermediate precision of the method. (n=8). Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min).

	Retention time			Area Counts		
Compound	**Average**	**Std Dev**	**%RSD**	**Average**	**Std Dev**	**%RSD**
Hexachloro-1,3-Butadiene	12.267	0.011	0.092	5339066	169231	3.170
Pentachlorobenzene	16.839	0.003	0.018	7928164	365144	4.606
Trifluralin	19.288	0.013	0.065	2573171	30306	1.178
Hexachlorobenzene	19.934	0.009	0.043	7234417	259060	3.581
Simazine	20.367	0.008	0.040	5036650	90501	1.797
Atrazine	20.574	0.011	0.055	5297335	143776	2.714
Lindane	20.871	0.006	0.027	7537697	318113	4.220
Caffeine	22.491	0.008	0.034	6228843	200569	3.220
Alachlor	23.920	0.008	0.033	6513196	258212	3.964
Aldrin	25.305	0.012	0.048	6719818	165020	2.456
Chlorpyrifos	25.839	0.007	0.026	4402964	163048	3.703
Isodrin	26.653	0.011	0.041	6411797	150841	2.353
Clofenvinfos	27.894	0.009	0.033	2477732	102498	4.137
Endosulfan I	29.017	0.006	0.021	6032069	197499	3.274
Dieldrin	30.467	0.013	0.043	5548832	159870	2.881
Endrin	31.678	0.010	0.031	6046668	207162	3.426
DEHP	35.213	0.005	0.014	5094766	234914	4.611

It can be seen above (Table 2.17 and Table 2.18) that precision was obtained in relation to both the retention time and also area counts of each target analyte were favourable. In no case was the relative standard deviation above 5% which is considered a precise result.

2.3.2.5.2 LINEARITY

A linear relationship should be evaluated across the range of the analytical procedure. It may be demonstrated directly by dilution of a standard solution containing target analytes and/or separate weighing of each stock standard. The linearity of an analytical procedure is its ability (within a given range) to obtain test results which are directly proportional to the concentration (amount) of analyte in the sample.

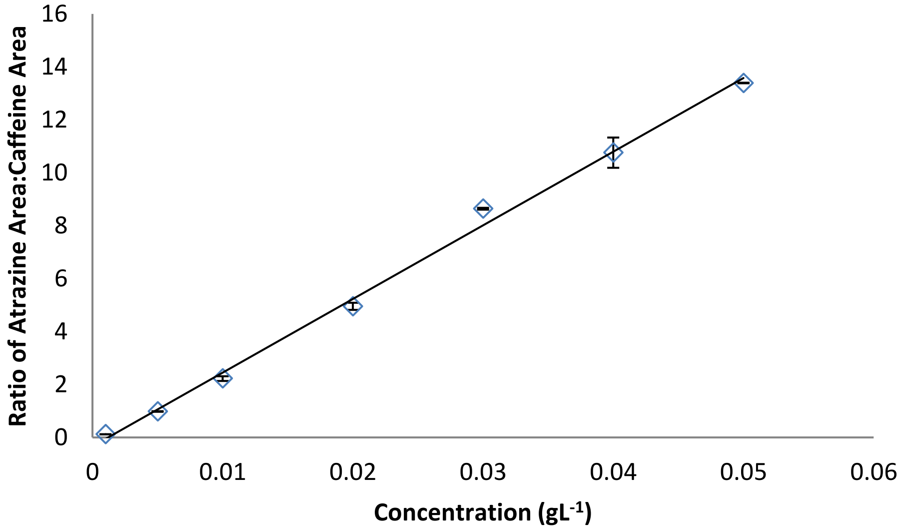


Figure 2.16: Calibration curve showing the linearity of atrazine from a range of 0.05-0.001 gL^{-1} after analysis on the GC-MS. The equation of the line (y=278.25x – 0.3342) and the r^2 value (0.9963) are also given. (Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min))

Within a calibration curve the measured slope should show a clear correlation between instrumental response and the analyte concentration. The results obtained should not show a significant deviation from linearity. This can be shown by looking at the correlation coefficient (r^2). If the correlation coefficient is above 0.95 the regression is deemed to be a good fit, as can be seen above in the calibration curve for atrazine (Figure 2.16). It can be seen below (Table 2.19) that all correlation coefficient values were demonstrated to be above 0.99 showing that the linearity of each of these target analytes was precise.

Table 2.19: Overview of calibration curves using internal standard method. (Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min))

Retention Time		Slope	Intercept	R^2
12.27	Hexachloro-1,3-butadiene	236.773	-0.163	0.9966
16.84	Pentachlorobenzene	342.407	-0.205	0.9934
19.29	Trifluralin	165.653	-0.511	0.9915
19.93	Hexachlorobenzene	329.523	-0.132	0.9947
20.37	Simazine	253.259	-0.441	0.9986
20.57	Atrazine	275.393	-0.379	0.9987
20.87	Lindane	298.713	-0.143	0.9964
23.92	Alachlor	290.945	-0.574	0.9957
25.3	Aldrin	321.924	-0.292	0.9980
25.84	Chlorpyrifos	273.404	-0.623	0.9983
26.65	Isodrin	273.073	-0.047	0.9990
27.89	Clofenvinfos	175.582	-0.478	0.9922
29.02	Endosulfan I	267.819	-0.256	0.9997
30.47	Dieldrin	244.741	-0.236	0.9995
31.68	Endrin	279.301	-0.338	0.9989
35.21	DEHP	352.325	-1.11	0.9912

2.3.2.5.3 LIMIT OF DETECTION (LOD) AND LIMIT OF QUANTITATION (LOQ)

The detection limit (LOD) of a method is the lowest amount of analyte in a sample which can be detected but not necessarily quantitated as an exact value (23). The quantitation limit (LOQ) of a method is the lowest amount of analyte in a sample which can be quantitatively determined with suitable precision and accuracy (24).

Table 2.20: Limits of detection and limits of quantification for all pesticides tested within the method when analysed using TIC mode. (Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min))

R. Time	Compound	LOD (mgL^{-1})	LOQ (mgL^{-1})	MAC Fresh water (µgL^{-1})	MAC Marine water (µgL^{-1})
12.267	Hexachloro-1,3-butadiene	0.056	0.187	0.6	0.6
16.839	Pentachlorobenzene	0.079	0.262	n/a	n/a
19.288	Trifluralin	0.089	0.297	n/a	n/a
19.934	Hexachlorobenzene	0.071	0.235	0.05	0.05
20.367	Simazine	0.036	0.120	4	4
20.574	Atrazine	0.035	0.117	2	2
20.871	Lindane	0.058	0.193	0.04	0.02
23.920	Alachlor	0.063	0.210	0.7	0.7
25.305	Aldrin	0.043	0.143	n/a	n/a
25.839	Chlorpyrifos	0.040	0.134	0.1	0.1
26.653	Isodrin	0.030	0.101	n/a	n/a
27.894	Clofenvinfos	0.085	0.285	0.3	0.3
29.017	Endosulfan I	0.018	0.060	0.01	0.004
30.467	Dieldrin	0.022	0.072	n/a	n/a
31.678	Endrin	0.032	0.105	n/a	n/a
35.213	DEHP	0.105	0.351	n/a	n/a

The MAC values are obtained from the Irish EPA and have been shown previously in Chapter 1 (Table 1.1) (137). Not all of the PPs were assigned MAC values. In some cases (PAHs and Diels-Alder based pesticides – dieldrin etc.) were considered together for the AA concentrations obtained. In all cases with the exception of Endosulfan when a 500 mL aliquot of water (selected from volume breakthrough studies (Section 2.3.1.4.1)) is cleaned up and pre-concentrated using the SPE method described previously (Section 2.3.1.3) the pesticides mentioned above are able to be detected at LOD or LOQ level.

2.3.2.5.4 RANGE

The range of a method is the interval between the upper and lower concentration of analyte in the sample for which it has been demonstrated that the method has a suitable level of precision, accuracy and linearity. The range of linearity is checked by injections of 5-6 concentrations of the reference standards (in triplicate) below and above the expected concentration of the samples to be analysed.

Table 2.21: Range of method for selected pesticides using TIC analysis. (Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min))

R. Time	Compound	Lower Concentration (mgL^{-1})	Upper Concentration (mgL^{-1})
12.267	Hexachloro-1,3-butadiene	0.187	10
16.839	Pentachlorobenzene	0.262	10
19.288	Trifluralin	0.297	10
19.934	Hexachlorobenzene	0.235	10
20.367	Simazine	0.120	10
20.574	Atrazine	0.117	10
20.871	Lindane	0.193	10
23.920	Alachlor	0.210	10
25.305	Aldrin	0.143	10
25.839	Chlorpyrifos	0.134	10
26.653	Isodrin	0.101	10
27.894	Clofenvinfos	0.285	10
29.017	Endosulfan I	0.060	10
30.467	Dieldrin	0.072	10
31.678	Endrin	0.105	10
35.213	DEHP	0.351	10

Standards of various concentrations were analysed using the GC-MS method in a range of 10 mgL^{-1} to an average lower concentration (LOQ value) of 0.179 mgL^{-1} for each analyte. During linearity studies, which have been mentioned previously (Section 2.3.2.5.2) it had been shown that good correlation values were obtained for each of the pollutants tested.

2.3.2.5.5 ROBUSTNESS

The robustness of a method is a measure of its capacity to remain unaffected by small but deliberate variations in method parameters and can provide an indication of its reliability during normal usage. Some variations that can be tested are the stability of analytical solutions, change of analytical columns (lots or suppliers), change in temperature or changes in flow rate.

The robustness of this method was looked at using two variables; injection port temperature and flow rate. The temperature of the GC injection port must be high enough to vaporize a liquid specimen instantaneously. If the temperature is too low, separation is poor and broad spectral peaks chould result or no peak develops at all. If the injection temperature is too high, the specimen may decompose or change its structure. If this occurs, the GC results will indicate the presence of compounds that were not in the original specimen.

Table 2.22 Relative standard deviation results of four parameters; retention time, area count, width and resolution of peaks when the injection port temperature was varied from 260°C, to 270°C, 265°C, 255°C and 250°C.

		% RSD (n=15)			
Average Retention time	Compound	Retention time	Area Count	Width	Resolution
12.27	1,3-Butadiene, 1,1,2,3,4,4-hexachloro	0.00	9.40	0.00	
16.85	Pentachlorobenzene	0.03	10.25	5.50	2.90
19.30	Trifluralin	0.04	13.56	8.70	6.65
19.95	Hexachlorobenzene	0.04	10.42	3.92	4.02
20.41	Simazine	0.02	9.17	7.99	7.04
20.60	Atrazine	0.04	9.08	0.00	3.18
20.89	Lindane	0.03	10.18	5.83	4.48
22.50	Caffeine	0.02	12.10	8.91	1.98
23.94	Alachlor	0.02	10.11	0.00	3.49
25.32	Aldrin	0.03	9.57	5.10	2.95
25.85	Chlorpyrifos	0.03	10.84	5.10	0.00
26.67	Isodrin	0.03	9.38	8.32	6.45
27.92	Clofenvinfos	0.05	13.60	8.32	7.59
29.04	Endosulfan I	0.03	9.79	6.98	6.80
30.49	Dieldrin	0.03	9.86	2.60	2.22
31.70	Endrin	0.03	10.38	5.55	1.39
35.22	DEHP	0.00	12.68	3.50	4.68

The above data (Table 2.22) shows that when the injector port temperature was altered a slight change in some of the chromatographic parameters being measured was observed. The parameter that showed the least variance was the retention time of the compounds, whilst the parameter with the most variance was the area count of the target analytes. As mentioned previously an increase in injector port temperature can lead to decomposition of the analyte or broad spectral peaks. Both these factors can be observed when looking at the variance in values obtained in relation to the area count and width of peaks within the resulting chromatograms.

The resolution values for both parameters were calculated for the peak of interest with the peak eluted prior (Table 2.22 and Table 2.23) e.g. it can be seen below that a value for pentachlorobenzene is shown (2.90) for the %RSD of the resolution (Table 2.22). This value is based on the resolution values for 1,1,2,3,4,4-heaxachlorobenzene-1,3-butadiene and pentachlorobenzene.

Table 2.23: Relative standard deviation results of four parameters; retention time, area count, width and resolution of peaks when the flow rate was varied from 1.1 mLmin^{-1}, to 0.9 mLmin^{-1}, 1.0 mLmin^{-1} and 1.2 mLmin^{-1}.

		% RSD			
R.T.	***Compound***	R.T.	Area	Width	Resolution
12.36	*1,3-Butadiene, 1,1,2,3,4,4-hexachloro*	1.77	11.55	40.22	
16.95	*Pentachlorobenzene*	1.43	20.21	23.09	29.05
19.42	*Trifluralin*	1.49	30.37	7.42	13.36
20.09	*Hexachlorobenzene*	1.65	20.51	15.03	39.62
20.50	*Simazine*	1.23	64.73	14.40	26.53
20.69	*Atrazine*	1.23	27.72	3.28	10.44
20.95	*Lindane*	1.16	29.30	7.41	15.11
22.24	*Caffeine*	2.56	30.25	14.53	52.19
23.74	*Alachlor*	2.00	30.05	14.40	10.81
25.14	*Aldrin*	1.81	31.75	6.08	12.18
26.03	*Chlorpyrifos*	1.66	31.73	3.28	7.30
26.86	*Isodrin*	1.75	28.28	9.90	6.16
28.10	*Clofenvinfos*	1.64	33.27	5.55	7.67
29.26	*Endosulfan I*	1.79	28.33	8.45	4.42
30.73	*Dieldrin*	1.86	26.58	2.82	2.32
31.85	*Endrin*	1.40	26.09	13.24	10.26
35.29	*DEHP*	0.48	29.94	16.03	7.93

The flow rate of the gas influences how fast a compound will travel through the column; the faster the flow rate, the lower the retention time. Generally, the flow rate is held constant throughout a run. When the flow rate of the carrier gas was altered more of an inconsistency was observed in the retention time, this is due to the travelling of the compounds on the column. However the %RSD still remained below 2.6 so this was considered a successful result.

2.3.2.6 ANALYSIS OF ENVIRONMENTAL SAMPLES ON GC-MS

The River Tolka is one of the three main rivers in County Dublin, and flows from County Meath to Fingal on the north side of Dublin City. By flow of water, the Tolka is the second largest river in Dublin but flows at a slower rate than the River Dodder. The rivers path through Dublin City takes it through a number of parks, and it initially passes through Tolka Valley Park, where it is the source of water for a natural pond that featured considerable bird life (26). The River Tolka has many tributaries, including the Hampstead Stream, which is in the surrounding area of Dublin City University (DCU). Previous work had been carried out within the research group with the River Tolka and permission had been obtained for sampling at this site.

A water sample was taken from the Tolka in February of 2008. These water samples were separated into 'spiked' and 'unspiked', and preconditioned by a factor of 500 using the SPE method outlined in a previous section (Section 2.3.1.3).

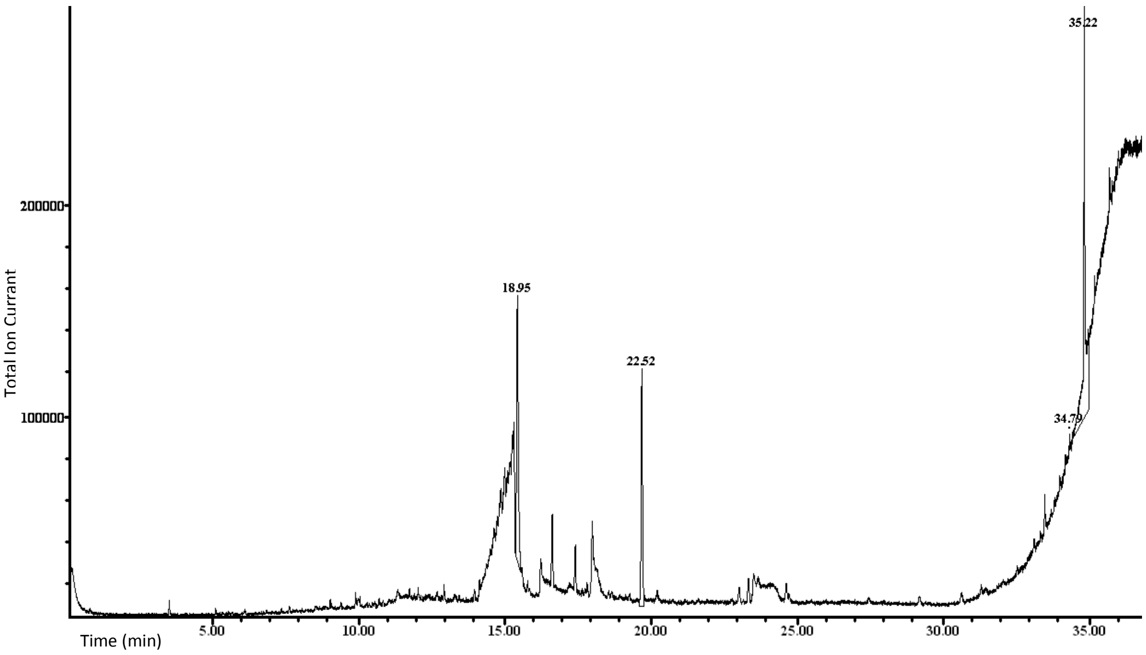


Figure 2.17: GC chromatogram of an unspiked water sampler obtained from the River Tolka (13th February 2008) following sample clean up and 500 fold preconcentration. SPE was carried out with Strata X cartridge (6 mL, 500 mg) with the following method; Conditioning 6 mL methanol, 6 mL DI H_2O; Rinsing 6 mL DI H_2O; Elution 1 mL acetonitrile, 1 mL isopropyl alcohol, evaporated down and reconstituted with 1 mL of acetonitrile. Samples were analysed using GC-MS. (Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min))

In the unspiked sample three analytes were identified using the MS software (Library: NIST98) (Figure 2.17). These were n-diphenyl methylene(diphenyl) methanamine (CAS 5350-59-4, 18.95 min); caffeine (CAS 58-08-2, 22.52 min) and DEHP (CAS 117-81-7, 35.22) min.

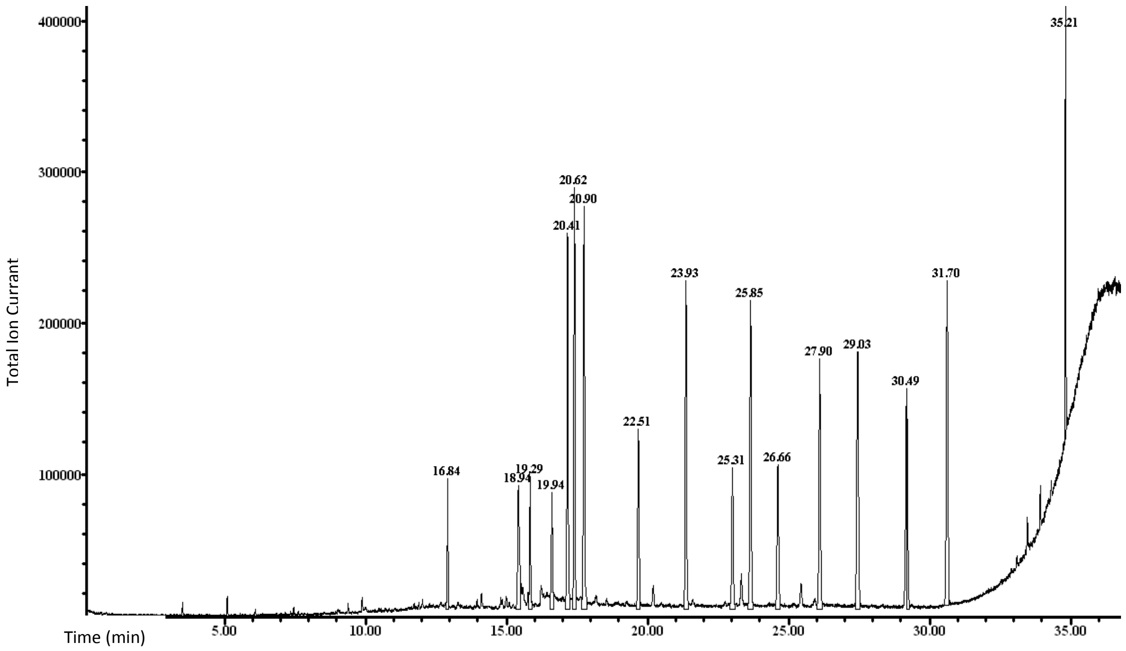


Figure 2.18: : GC chromatogram of an spiked water sampler obtained from the River Tolka (13th February 2008) following sample clean up and 500 fold preconcentration. SPE was carried out with Strata X cartridge (6 mL, 500 mg) with the following method; Conditioning 6 mL methanol, 6 mL DI H_2O; Rinsing 6 mL DI H2O; Elution 1 mL acetonitrile, 1 mL isopropyl alcohol, evaporated down and reconstituted with 1 mL of acetonitrile. Samples were analysed using GC-MS. (Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min))

When looking at the spiked sample, one can see all of the peaks that are relative to the pesticide sample (Figure 2.18). When analysing the results it was noted that the concentration of DEHP in the spiked sample was increased, alongside peaks at 16.84 min (pentachlorobenzene) and 19.95 min α Lindane. These concentrations while detected still fell below the MAC set down for the target analytes.

2.3.3 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

A method was developed for HPLC for screening of novel passive sampling materials during their development stage. This method does not encompass as many target analytes as the GC-MS method detailed above (Section 2.3.2) as it was developed to operate as a short timed screening method in the testing of SPE procedures and the development and screening of novel passive sampling devices.

2.3.3.1 INSTRUMENTATION

Liquid chromatographic analysis was performed with an Agilent Technologies Liquid Chromatograph (Little Island, Cork, Ireland), equipped with HPLC pump (Agilent 1100 series), auto sampler (Agilent 1100 series), VWD detector (Agilent 1200 series), injection valve (injection volume: 20 µL). The separation was carried out using a C18, 5 µm Luna column (250 mm x 4.6 mm I.D., Phenomenex, CA, USA)

2.3.3.2 ATRAZINE AND DIELDRIN METHOD

A simple method was needed for the quick determination of both atrazine and dieldrin as these are the main compounds that are used in the determination of optimum methods and were also used for further studies in the development of passive samplers (Chapter 3) and the development of the SPE method (Section 2.3.1). This method was required for several reasons, one being that the run time for the GC-MS method is 40 minutes long, and also for ease and speed of analysis.

Standards of both compounds were made up in acetonitrile, and injected onto a C18 column. The mobile phase used was 95:5 acetonitrile: DI water, and the run time was below 8 minutes.. Chromatographic parameters for this method are detailed in the sections below.

2.3.3.2.1 ADDITION OF FLUORANTHENE IN ANALYSIS

For the analysis of novel passive sampling materials detailed in Chapter three, fluoranthene was added to the target analytes atrazine and dieldrin. This was done for two main reasons, to show that these samplers not only had the ability to be used for analysis of pesticides in aqueous environments but also had the ability to sample for other organic pollutants that can be found in environmental samples.

When looking at chemical and physical properties of fluoranthene, it was found to have properties intermediate to those of atrazine and dieldrin as is tabulated in Chapter 3.

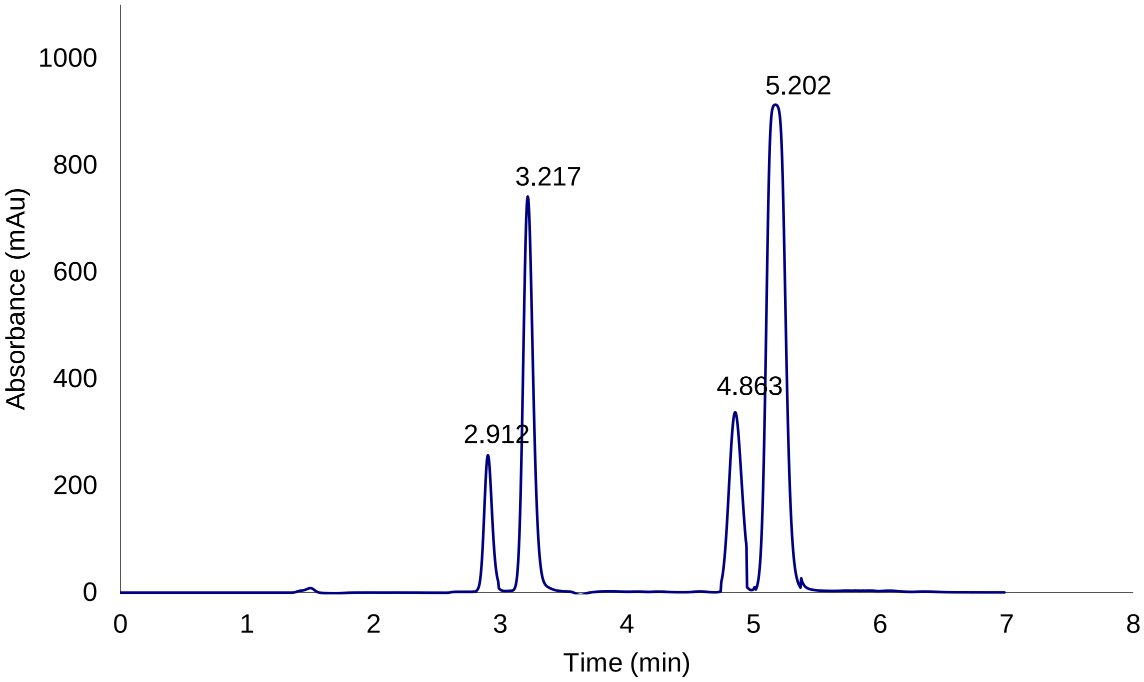


Figure 2.19: Chromatogram of first HPLC method for the testing of methods and novel sampling materials. Mobile phase 95:5 ACN: DI H^2O, Wavelength 215 nm, flow rate 1.0 $mLmin^{-1}$. Peak Identification: 2.912 min Caffeine (IS), 3.217 min Atrazine, 4.863 min dieldrin and 5.202 min Fluoranthene.

A calibration curve was carried out for the three PP's shown in the chromatogram above (Figure 2.19). The tabulated data below (Table 2.24) shows both the slope and intercept of the calibration curves and the correlation value and range of these slopes.

Table 2.24: Results obtained from calibration curve (Internal Standard Method) of PPs using test method one. The samples were analysed using a C18 (250 mm x 4.6 mm ID 5 µm Luna column, mobile phase 95:5 v/v acetonitrile:water.

Analyte	Slope	Intercept	R^2	Range (mgL^{-1})
Atrazine	0.978	0.5468	0.995	0.05 – 7
Dieldrin	0.091	0.0714	0.958	0.5 – 7
Fluoranthene	9.368	2.8936	0.981	0.25 – 7

As can be seen each of these calibration curves show a high level of linearity and a fall within a range that was used for testing of the analytes. A series of chromatographic parameters were calculated for the above method and are discussed herein.

For the parameters α (Relative retention) and Rs(w) (Resolution using baseline width), the values deal with the peak in question and the peak directly above it; e.g. α of Atrazine = 1.21, this is the relative retention between atrazine and caffeine.

Table 2.25: Calculated chromatographic properties for test method one. The samples were analysed using a C18 (250 mm x 4.6 mm ID 5 µm Luna column, mobile phase 95:5 v/v acetonitrile:water.

	t'R	α	k'	Rs (w)	N (w)	H (w) (cm)
Caffeine	1.40		0.93		5292.6	0.0047
Atrazine	1.70	1.21	1.12	1.66	4121.6	0.0061
Dieldrin	3.35	1.97	2.22	7.50	6561.0	0.0027
Fluoranthene	3.69	1.10	2.44	1.31	5518.4	0.0043

Adjusted retention time (t’R) is the retention value that is obtained by subtracting the dead time from the total retention time. This is the time that the compound spends in the stationary phase.

The relative retention time (α), is the ratio between the net retention time of a substance and that of a standard compound. The value of α must always be larger than one. Relative retention time is relatively independent of flow rate and can therefore be used to aid in the identification of peaks with flow rate changes (22).

Capacity factor (k') is often the parameter used to describe the migration rate of analytes on a column (27). The retention factor for any analyte is obtained by division of the adjusted retention time by the dead time value. When an analytes retention factor is less than one, elution is considered so fast that the determination of retention time can be difficult. Ideally the retention factor for an analyte should be between one and five. As can be seen from the values above (Table 2.25) all but caffeine fall within this range and caffeine is only marginly below (0.93).

Another method of determining how well different analytes are separated is through the resolution measurement. Resolution can be calculated using the baseline width of the peak (w). The resolution of the two analytes is defined below, with baseline resolution being achieved when R is equal to or greater than 1.5 (22).

$$RR = \frac{2(tr_2-tr_1)}{ww_1+ww_2}$$

(Eqn. 2.4)

It can be seen above that the resolution between all peaks but dieldrin and fluoranthene are above 1.5 (Table 2.25). While the value obtained was close (1.31) it should be noted that in none of the laboratory based tests analysed on the HPLC that these two compounds were analysed together.

A theoretical plate (N) is a hypothetical stage in which two phases establish equilibrium with each other. The greater the number of theoretical plates the greater the efficacy of the separation process. A column that has a high number of theoretical plates will have a narrower peak at a given retention time than a column that has shown a lower plate number. Column efficiency is a function of the column dimensions and is often measured in N/m for comparison purposes. N can be calculated using the following formula:

$$NN = 16\left(\frac{Rt}{w}\frac{Rt}{W}\right)^2$$

(Eqn. 2.5)

To calculate the height of the theoretical plate one divides the length of the column by the number of plates and will obtain the height of the theoretical plates.

This HPLC test method was used extensively not only within this chapter, for optimization of the SPE process, but also in Chapter 3 for the screening of novel sampling materials and then again for the tuning of novel samplers.

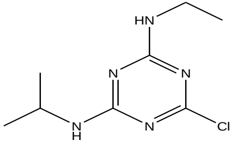
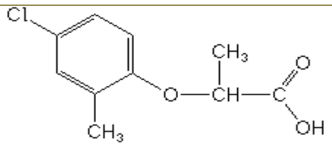
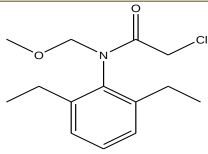
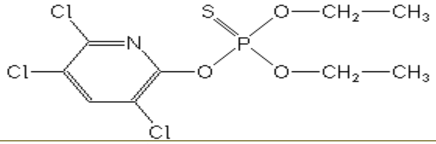
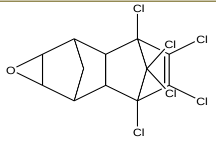
2.3.3.3 HPLC METHOD FOR PESTICIDE MIX

This HPLC method was developed to analysis the enrichment of pesticides into novel passive samplers (Section 3.3.3.4). Five pesticides, alachlor, atrazine, chlorpyriphos, endrin and mecoprop, were selected for this study. All with the exception of mecoprop are priority pollutants mentioned in Annex X of the WFD.

Mecoprop or methylchlorophenoxypropionic acid (MCPP) is a commonly used general use herbicide found in many household weed killers, and mainly used to target broadleaf weeds. Mecoprop is not regulated by the WFD or its daughter regulations, but has been included in the monitoring programme of the Irish EPA. Mecoprop was mentioned in Appendix 2.1 of the EPA water WFD monitoring program as a relevant pollutant.

Within the tabulated data below (Table 2.26) structures of the five pesticides are given alongside their relevant physicochemical properties.

Table 2.26: Five pesticides analysed in this method with selected physicochemical properties (Analytical parameters: Mobile phase 70:30 ACN:DI H_2O, wavelength 210 nm, flow rate 1.0 mlmin^{-1}. Peak identification 2.30 min mecoprop, 4.91 min atrazine, 9.40 min alachlor, 10.60 min endrin and 24.55 min chlorpyriphos.)

Name of priority substance	*Structure*	*molecular weight (gmol^{-1})*	*molecular formula*	*Log K_{ow}*
Atrazine		215.68	$C_8H_{14}ClN_5$	2.61
Mecoprop		214.6455	$C_{10}H_{11}ClO_3$	2.84
Alachlor		269.77	$C_{14}H_{2}0ClNO_2$	3.5
Chlorpyriphos		350.6	$C_9H_{11}Cl_3NO_3PS$	4.77
Endrin		380.91	$C_{12}H_8Cl_6O$	5.2

Standards of all compounds were made up in acetonitrile, and injected onto a C18 column. The mobile phase used was 70:30 acetonitrile water. Separation of the first four analytes occurred with good resolution within eleven minutes however chlorpryiphos did not elute until 25.5 min as can be seen below (Figure 2.20).

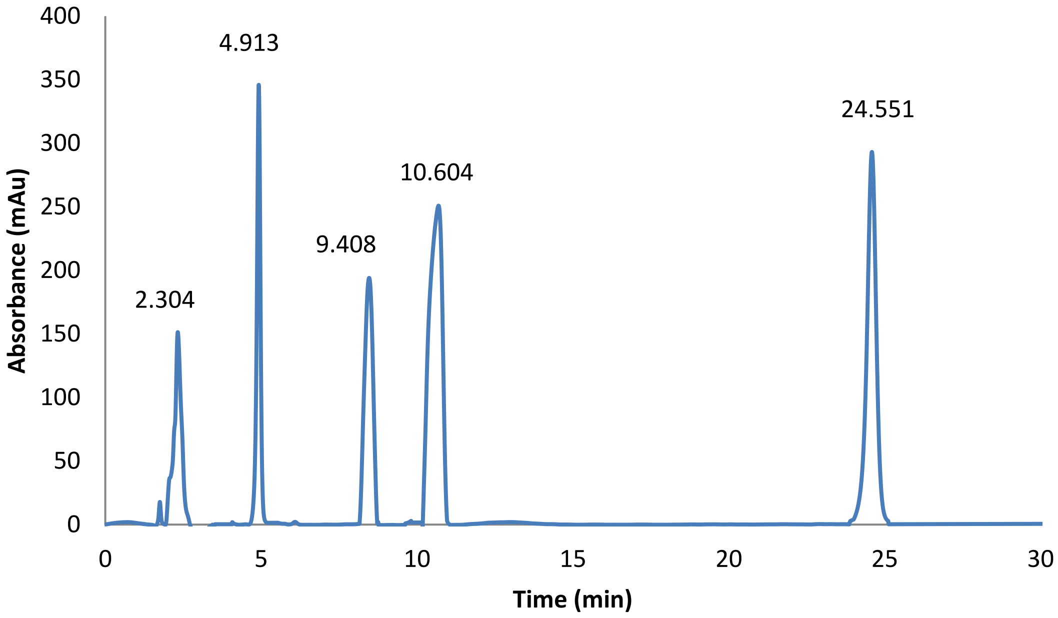


Figure 2.20: Chromatogram showing HPLC separation. Analytical parameters: Mobile phase 70:30 ACN:DI H_2O, wavelength 210 nm, flow rate 1.0 mlmin^{-1}. Peak identification 2.30 min mecoprop, 4.91 min atrazine, 9.40 min alachlor, 10.60 min endrin and 24.55 min chlorpyriphos.

A calibration curve was constructed for each of the four analytes. In the tabulated data below both the slope and intercept of the calibration curves and the correlation value and range of these slopes (Table 2.27). All five of these calibration curves show good linearity and high correlation values.

Table 2.27: Results obtained from calibration curves of target analytes analysed using HPLC. Analytical parameters: Mobile phase 70:30 ACN:DI H_2O, wavelength 210 nm, flow rate 1.0 mlmin^{-1}

	Slope	Intercept	R^2 value	Range (mgL^{-1})
Atrazine	2,321,655	3,125,853	0.983	0.05-15
Mecoprop	1,309,309	3,617,006	0.978	0.2-15
Alachlor	1,671,936	1,726,374	0.998	0.1-15
Endrin	577,900	4,600,344	0.979	0.1-15
Chlorpyriphos	1,364,191	2,199,688	0.984	0.07-15

As seen with the previous method (Section 2.3.3.2) chromatographic parameters were calculated and can be seen tabulated below.

Table 2.28: Calculated chromatographic properties for pesticide mix method. Analytical parameters: Mobile phase 70:30 ACN:DI H_2O, wavelength 210 nm, flow rate 1.0 mlmin^{-1}

	t'R	α	k'	Rs (w)	N (w)	H (w) (cm)
Mecoprop	1.834		3.902		217	0.1149
Atrazine	4.443	2.4225	9.453	5.00	2225	0.0112
Alachlor	8.933	2.0105	19.006	8.69	4593	0.0054
Endrin	10.134	1.1344	21.562	1.7301	25923	0.0096
Chlorpyriphos	24.081	2.376	51.236	17.465	16530	0.0015

As with previous table (Table 2.25) for the relative retention and resolution values, the numerical values given correspond to the peak in question and the peak directly above it e.g. α Atrazine = 2.4225, this is the relative retention between atrazine and mecoprop.

In comparison to the previous HPLC method used the capacity factor values for this method were much higher. Capacity factor values of 20 or larger indicates that the elution is one which will take a long period of time. The values obtained for alachlor and endrin show a k’ of 19.006 and 21.562 respectively, while the value of chlorpyriphos is higher at a value of 51.236. This indicates that these three compounds are retained by the column for a longer length of time than that mecoprop and atrazine. One issue encountered in the development of this test method was the use of an isocratic pump with the HPLC. If a gradient pump had been available for use it would have been possible to have altered the separation with the aim of decreasing the run time.

2.4 CONCLUSIONS

The development of sample preparation and analytical methods was an integral part of this project. As mentioned in the aims and objectives the sample preparation method that was chosen was a quite common form; SPE. This is a useful technique as it not only cleans up the sample but can also allow for pre-concentration of the target analytes. When looking at the possible sorbents it was found the polymeric sorbents showed the best results and Strata X was chosen. There are several type of sorbent bed sizes commercially available, but it was decided to use a large size (500 mg) to allow for large volumes of water, which is now becoming common practice with environmental samples. The final method for sampler preparation used a Strata X (6 mL 500 mg) cartridge, conditioned with methanol and water, and eluted with acetonitrile and isopropyl alcohol. After the breakthrough volume was determined it was decided that environmental sample volumes were analysed using 500 mL.

Two analytical instruments were used for the testing and screening of novel passive sampling materials; both GC and HPLC. The method developed for GC was more detailed as this was to be more sensitive for LODs and LOQs and would be used for environmental samples. The GC also used a MS detector which was critical in the running of environmental samples, both the Tolka Water sample that was seen within this chapter, and was also an essential part of the analysis of deployed sampling materials and water samples analysed in chapter 6, for the identification of compounds. The final GC methods temperature programme was as follows ; initial temperature 40^{o}C (hold 2 min), 9 ^{o}Cmin^{-1} to 170 ^{o}C, 3 ^{o}Cmin^{-1} to 205 ^{o}C, 1^{o}Cmin^{-1} to 208 ^{o}C, 20 ^{o}Cmin^{-1} to 290 ^{o}C (hold 2 min) with a run time of 36 min. All but two peaks, (hexachlorobenzene and atrazine) showed peak resolution of above 1.5.

Of the two HPLC methods developed, the most commonly used one was Test Method One. The run time of this method was very short and this allowed for the rapid determination during the development and screening process of the polymeric materials, which can be seen in more detail in both Chapter 3 and 4. While the second HPLC method had a longer run time, this method was only used for one study, the enrichment of pesticides into novel sampling materials and can be seen in more detail in Chapter 3. While the HPLC methods did not show the same levels of sensitivity as that of the GC, an important point to note is that these methods were used for screening and development and as such it was possible to use greater concentrations of pollutants than what would be seen in the environment.

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CHAPTER 3: DEVELOPMENT OF NOVEL PASSIVE SAMPLERS BASED ON PLASTICISED PVC.

3.1 INTRODUCTION

A plasticiser is a material that can be added to a polymer to give the resulting polymeric material increased softness and flexibility. This is due to the fact that istlowers the second order transition temperature of the material. Plasticisers are low molecular weight resins or liquids, which will form secondary bonds to polymer chains and in turn spread them apart. Thus, plasticisers reduce the polymer-polymer chain secondary bonding and provide more mobility for the macromolecules, which will result in a softer, more easily deformable mass (1). Through the introduction of a plasticiser the range of applications for any given polymer can be increased to include applications within the automotive industry, medical and consumer products (2). In recent times research of plasticisers has be focused on leaching, degradation, evaporation and migration (2).

It is important that the plasticiser should be compatible with the polymer (3), that is to say that it should be completely miscible and remain permanently within the polymer. In general, this requires that the polymer and plasticiser should have solubility parameters within one or two units of each other (4). Low molecular weight will favour miscibility and having strong mutual hydrogen bonding is a secondary factor that will aid in the compatibility of polymer and plasticiser (5).

When a plasticiser meets these requirements, it will in turn act as a solvent for the polymer and can speed melt processing (5). In cases where the solubility parameters are slightly further apart, the plasticiser will need to be heated in order to dissolve the polymer. In these cases on cooling down to room temperature, the material forms a gel. This may in turn favour optimum balance of flexibility and strength. If the solubility parameters are even further apart, the plasticiser and polymer combination will be incompatible unless used in combination with a compatible ‘primary’ plasticiser, in which case the initial plasticiser would be considered a ‘secondary’ plasticiser.

Plasticisers decrease the glass transition temperature (Tg) (6) and thereby influence the melting and softening temperatures of polymers, alongside some mechanical properties e.g. the elastic modulus and hardness of polymers. Most of the plasticisers can change the degree of softness of polymers over a wide range depending on the type and quantity added

PVC is one of the more unique polymers available on the market today due to its ability to accept high levels of plasticiser (up to 100 parts per hundred of resin (phr) (7)) (8) whilst still retaining useful mechanical properties. This can be attributed to regions of order (microcrystalline) within a predominantly amorphous polymer structure, being reduced but not eliminated by incorporation of the plasticiser. The plasticisers are held in solution by a dipolar attraction within the amorphous regions whilst the micro-crystallites provide elastic recovery from deformation due to the inter-chain association (9).

PVC has approximately 85% amorphous regions that have the ability to absorb plasticiser and produce flexibility, and 15% crystalline regions that remain firmly bonded and will retain strength and creep resistance. Due to this balance PVC is in use by about 80-90% of the total plasticiser market (9). The most commonly used plasticizing materials remain the phthalic acids. It has been found that linear alkyl phthalates are superior to branched phthalates in terms of both efficiency and permanence.

Plasticisers should be low molecular weight, and be high boiling, have low vapour pressure and should not migrate to the surface in order to avoid a later embrittlement of the softened products.

3.1.1 POLYMERS

Polymers are a group of chemical products which have a common building principle. They consist of macromolecules which are long chain molecules, that contain large numbers of smaller repeating groups (monomers). Molecules that consist of small numbers of monomers are often called oligomers. There are a variety of types of polymers; natural e.g. wool and silk, half synthetic e.g. chemically modified natural polymers like cellulose plastics and synthetic polymers.

Polymers can be linear, branched or cross linked in structure. Within these structures the polymer can be a homopolymer (one type of monomer) or a copolymer (different types of monomers). In the cases of copolymers the monomers can be arranged in several different combinations. Random copolymers have no regularity in the arrangement of the distinct monomers. Block polymers consist of blocks of oligomer A followed by blocks of oligomer B. Alternating copolymers is where the distinct monomers alternate within the composition of the material. The physico-chemical properties of the copolymer will be strongly influenced by the composition and arrangement of monomers within its structure.

Synthetic polymers, in comparison to natural polymers (e.g. DNA) have a certain distribution of molar mass and do not give a distinct molecular weight. The molar mass of synthetic polymers can range from some thousand gmol^{-1} to some million gmol^{-1} (10). Polymers when used in objects or films can be rigid, flexible, transparent, and weather resistant. A polymer is usually one of an option of materials that can be used for certain applications. Some of the advantages of polymer use include; optical transparency, ease of processing making the material suitable for casting in a variety of shapes and also can be a cost effective material.

The formation of synthetic polymers is a process which occurs via chemical connection of many hundreds up to many thousands of monomer molecules. The chemical process of chain formation may be subdivided roughly into two classes, depending on whether it proceeds as a chain growth or as a step growth reaction.

Chain Growth Polymerisations

Chain growth (addition) polymerisations are characterised by the occurrence of activated species (initiators). Typical initiators include any organic compound with a labile group. They add one monomer molecule after the other in a way that at the end of each new species formed by the monomer addition step, an active species is formed. From there the chain growth can start as a cascade reaction (propagation). Finally the growth of an individual macromolecule is arrested in either a termination or a transfer step (11).

While termination leads to the irreversible disappearance of an active centre, chain transfer results in the growth of a second chain while the first one is terminated. In this case the active centre is transferred to another molecule (solvent, monomer etc.) where it is able to initiate further growth. The resulting 'dead' polymer on the other hand can continue its growth only when activated in a subsequent transfer step. Due to the fact that this reactivation generally does not occur at the terminal monomer unit but instead at another place within the monomer chain, branched or cross linked products will result.

In summary, chain growth polymerisations are typical chain reactions involving a start up step (initiation), followed by many identical chain reaction steps (propagation) stimulated by the product of the first start up reactions. Transfer processes may continue until, finally, the active centre disappears in a termination step. Monomers that are appropriate for chain growth polymerizations either contain double or triple bonds or are cyclic, having a sufficiently high ring strain. Chain growth polymerisation is involved in the manufacture of polymers such as polyethylene, polypropylene and PVC.

Step Growth Polymerisations

In step growth polymerisations the monomers present do not have the specific activated centres to force the connection, and the process does not involve a cascade reaction. The monomers are instead tied together in discreet, independent steps via conventional organic reactions such as ester, ether or amide formation. Depending on where small molecules are released in the connection step the process can be distinguished between polycondensations (loss of small molecule) (12) and polyadditions. Monofunctional molecules cannot result in polymer chains via step growth polymerization, instead each monomer, and each intermediate molecule, must possess two functional groups. When there are more than two functional groups present on the monomer, branched or cross linked polymers will be formed (13).

Step growth polymerisations are categorised according to how the functional groups are assigned to the monomer. When each monomer bears two identical functional groups the process is called AABB-type polycondensation/polyaddition. Here mixtures of at least two different types of monomers are required, bearing the complementary function groups. If, on the other hand, each monomer molecule bears two complementary function groups required for the step grown polymerisation, the process is called AB-type polycondenation/polyaddition.

As a consequence of the lack of special active centres, the chain formation in step growth polymerisation occurs via a sequence of accidental and independent reaction events. It proceeds via dimers, short and longer oligomers until, finally at conversions higher than 99% long chains are formed which are called condensation polymers (polycondensates) or addition polymers. Many naturally occurring and some synthetic polymers are produced by step growth polymerization e.g. polyesters, polyamides and polyurethanes etc.

3.1.1.2 POLY (VINYL CHLORIDE) (PVC)

PVC is one of the most versatile plastics and is the second largest manufactured resin by volume worldwide (14), with current production exceeding 31 million tons per annum. PVC is relatively inexpensive and is used in a wide range of applications. It has found uses in most industrial sectors (e.g. packaging, building, and medical care)

PVC is a polymer that is prepared from vinyl chloride monomer (VCM), which in turn is produced by the thermal cracking of ethylene dichloride (EDC). The chlorine used in the manufacture of EDC is derived from common salt (NaCl) by electrolysis, so 43% by weight of PVC originates from crude oil (10). PVC is mainly produced as a homopolymer. PVC is a generic name for this polymer as each producer can make a range of PVC polymers which will vary in morphology and in molecular mass, depending on the intended end use. PVC due to the large chlorine atom, which imparts a strongly polar capability to the polymer chain, has a limited level of crystallinity (15).

PVC can be made more flexible through the addition of plasticisers, and in this form has found uses such as in clothing and upholstery.

3.1.1.2 ADDITIVES IN POLYMERS

An additive is a substance that is incorporated into a substance to achieve a technical effect in the finished product. Examples of additives include antioxidants, emulsifiers, plasticisers, and stabilisers. Plasticisers are added to improve processability of a polymer. PVC for example is typically a material whose usage is greatly determined by plasticisers and other additives. PVC is able to accept large levels of plasticisers' content while retaining useful mechanical properties.

A plasticiser is a chemical that can be used to reduce the stiffness of an amorphous thermoplastic resin. A plasticiser increases the molecular mobility of the polymer chains. The softening effect of plasticisers is a highly non linear function of the amount added, since the plasticiser acts to lower the glass transition temperature; however it should be noted that the stiffness does not change uniformly with concentration (16). Plasticisers are discussed in more detail in Chapter 4.

In unplasticised PVC a rigid film can be produced with strong interactions between neighbouring polymeric chains, which result in a rigid network. This gives the polymer its well characterised properties of rigidity, tensile and impact strength. When plasticised PVC is prepared, the plasticiser, due to their long alkyl chains will in effect screen the polymer chains from each other.This will inhibit them from reforming the chain to chain interactions that is observed in unplasticised PVC. It is important to note that there should be compatibility between the polymer and the plasticiser to ensure that the plasticiser is retained in the flexible final product.

3.1.1.3 APPLICATIONS

Polymeric materials can be used in simple household items like plastic bags as well as in advanced optical, electronic components, or in medical applications. PVC membranes doped with sebacate (17), phthalate (18) plasticisers were used in the sensing of metals. Studies have been carried out using plasticiser doped PVC for the determination of benzene, toluene, ethyl benzene and xylenes (BTEX) in water using infrared detection using a selection of plasticisers. Some plasticisers that have been looked at include di-2-ethylhexylsebacate, di-2-ethylhexyl phthalate (19) and 2-nitrophenyl-octyl ether. There have also been reports of the reusability of the sensing phase (20).

Buvailo *et al.* (21) presented work that was passed on polymers deposited as a thin film on a glass slide, with results being analysed using transmission FTIR spectroscopy. The research aimed to determine if these polymeric films were able to detect the water vapour adsoption-desorption responses through variation of relative humidity. These films were cast onto surface acoustic wave (SAW) humidity sensors, and it was found that the PVP-based coating demonstrated faster dynamics than the PVA coating. Through use of these films, and the ease and speed of FTIR analysis these sensors show great potential as commercial wireless humidity detectors.

St. George *et al.* (22) developed a passive sampling device based on a thin polymeric film. The polymer that was chosen was ethylene vinyl acetate (EVA). The film was cast at approx 1 µm and has found use as both an equilibrium and a kinetic sampler through variation of the thickness of the polymer coating. The EVA was coated on to Whatman glass fibre filters, prior to baking leaving a thin layer of polymer on the bead. These beads post deployment were removed and soaked in methanol for a 24 h period, which was then repeated prior to evaporation of the extracts down to 2 mL through use of a rotary evaporator. This sampler was deployed to determine the TWA of several pesticides mentioned in Annex X of the WFD.

Another use was published for polymeric thin films by Regan *et al.* (23) in 1996. The aim of their study was the development of an *in situ* optical sensor for the monitoring of pesticides in water. The sensor was an ATR (ATR) element or a silver halide optical fibre with a polymeric coating. The polymeric coating that was selected was PVC with a chlorparaffin plasticiser. This polymeric material was used to study the enrichment of chlorinated pesticides, atrazine and alachlor. It was observed that the pesticides were found to enrich within 20-30 min, however the detection limits that were reached were only 2 mgL^{-1}. While this may be useful for detection of high levels in accidental exposures or spillages, with the high levels of the LOD this would not yet be suitable for analysis of environmental standards for monitoring purposes.

Further work was carried out by Regan *et al.* (24) using PVC as the polymeric material, however in this study instead of the use of chloroparaffins as a plasticiser a selection of 10 different plasticisers were tested for the enrichment of toluene and tetrachloroethylene. It was observed that when the percentage composition of the plasticiser was increased an enhancement in analyte absorbance was noted. Within the article competitive interaction between the target pollutants was studied, it was found that when the analytes were enriching into the film competitively the enrichment time increased for all BTEX compounds with the exception of benzene.

A study preformed by Silva *et al.* (19) using a plasticised PVC membrane for the determination of BTEX concentrations in water. In this study it was shown that phthalate doped PVC membranes (150 µm thick) were used to determine the enrichment profile of BTEX compounds by IR. The plasticiser used was di-2-ethylhexyl phthalate (DEHP), and it was seen that with increasing the plasticiser concentration an increase in analyte concentration enrichment for BTEX compounds was seen. The addition of a plasticiser can change the affinity of the polymer membrane in relation to target analyte

As can be seen there is a wide range of applications for plasticised materials both in the literature and within industry. In this work the goal was to create an optically clear sampler which was robust enough to survive exposure to environmental conditions. Buvailo *et al.* (21) have shown applications of these materials on a smaller scale. Buvailo *et al.* cast their film on a glass slide, and while this will work within a research laboratory, the casting of this material would need to be altered for deployment within the environmental.

3.1.2 PLASTICISERS

There are two principle ways to obtain plasticisation effects that are commonly used and these are through use of internal and external plasticisers and are detailed below.

3.1.2.1 INTERNAL PLASTICISERS

Internal plasticisation is a process in which the plasticisation is produced by structural groups being incorporated into a polymer to lower the Tg (9). A rigid polymer may be internally plasticised by chemically modifying the polymer or monomer so that the flexibility of the polymer is increased. In certain cases the principle of 'internal' plasticisation is applied. In this case monomer units are built into the polymer chains, and will act as irregularities in the otherwise regular chain structures and in doing so causing a decrease in the Tg in comparison to that of the unmodified homopolymer. One advantage of 'internal' plasticisation is that the plasticising unit is chemically linked to the polymer so therefore cannot migrate. On the other hand one main disadvantage is that the number of plasticising monomers available is limited (25). For this reason internal plasticisation is used less frequently that external plasticisation which offers more variations.

3.1.2.2. EXTERNAL PLASTICISERS

It is possible that a rigid polymer can also be externally plasticised through the addition of a plasticiser, which in turn will impart flexibility, but is not chemically changed by the reaction with the polymer. The plasticiser molecules are taken up by the polymer particles and thereby they gel to the polymer by being inserted between the chain molecules of the macromolecular substances (25). In this form, 'external' plasticisers will reduce the interaction between the polymer chains which can be observed physically through the reduction in the glass transition temperature.

This method of plasticisation has the advantage in that it has lower cost than internal plasticisation and coveys a greater degree of freedom on the chemist to create differing flexibility by changing either the plasticiser group or concentration. External plasticisation is the more commonly used method for inducing flexibility into polymers as it is a long established technology which can be used on a large scale (9).

The work carried out in this chapter involves the incorporation of a series of external plasticisers into PVC not only to confer flexibility but also to determine the effect of the plasticiser on the enrichment of target pollutants.

3.1.2.3. PRIMARY PLASTICISERS

Primary plasticisers lower the Tg of the polymer whilst increasing the elongation and softness of the polymer. Primary plasticisers, if used in conjunction with secondary plasticisers, enter the polymer systems first. Plasticisers entering the crystalline regions of crystalline or semi crystalline polymers are referred to as primary plasticisers. If the amorphous regions of these polymers are penetrated, the plasticiser may be considered as a solvent type plasticiser (26).

3.1.2.4. SECONDARY PLASTICISERS

Secondary plasticisers (also known as extenders) do not bring about the changes that are seen with the addition of primary plasticisers when added to the polymer alone. However when secondary plasticisers are added to a polymer already containing a primary plasticiser the plasticising ability of the primary plasticiser is enhanced. Secondary plasticisers would not penetrate the original polymer-only system and are used as diluents for primary plasticisers.

The most commonly used secondary plasticisers are chlorinated hydrocarbons, which are chlorinated to varying amounts (typically 30-70%). For a given hydrocarbon plasticiser viscosity increases with increasing chlorine content. The principal advantages of such materials are that they improve fire retardancy by merit of their chlorine content, and formulations that contain a secondary plasticiser are often cheaper (27).

3.1.3 MECHANISM OF PLASTICISER ACTION

How external plasticisers effect their changes in PVC has been a matter of conjecture and a subject of research since the 1940s (28). Several theories of plasticiser action have been proposed, ranging in their detail and complexity. While each of the below mentioned theories is not exhaustive, it’s possible to gain an understanding of the plasticisation process by combining select ideas from each of the below theories (27).

3.1.3.1 THE LUBRICITY THEORY

This theory, developed by Kilpatrick, Clark and Houwink (28) is based on the assumption that the rigidity of the resin arises from molecular friction binding the chains together in a rigid network. It is based on the principle that the plasticiser in the PVC will act as a molecular lubricant that in turn allows the polymeric chains to move freely over one another when a force is applied to the plasticised material (28). Once the material is heated, these frictional forces are weakened and therefore will allow the plasticiser molecules to move between the chains. As such once this mixture reaches room temperature the plasticiser molecules act as lubricants for the polymer chains (27). In this model it is assumed that one portion of the plasticiser is strongly attached to the polymer, whilst the other segments are not. The former acts as a solvent for the polymer while the latter acts as a lubricant (29).

3.1.3.2 THE GEL THEORY

The gel theory of plasticisation was developed by Aiken and others and it extends on the lubricity theory (28) in that it deals with the idea that the plasticiser through breaking of the resin-resin bonds and interaction prevents their reformation by masking their centres of attachment. It holds that the polymer molecules are ‘tied’ loosely together at varying intervals. Through addition of a plasticiser, the random motions of the polymer chains will increase in the non-associated regions of the polymer.

This process while necessary can be considered by itself to be insufficient to explain a completely plasticised system because whilst a certain concentration of the plasticiser will provide plasticisation by this theory, the remainder will act more in accordance with the lubricity theory above, with unattached plasticisers molecule swelling the gel, and allowing for the movement of plasticiser molecules, which in turns imparts flexibility (27).

3.1.3.3 THE FREE VOLUME THEORY

The free volume theory of plasticisation sought to explain the reduction in polymer glass transition temperature upon the addition of plasticiser. Free volume is a measure of the internal space available in a polymer for the movement of the polymer chain, which imparts flexibility to the resin. It has been observed that the specific volume of polymers decreased linearly with decreasing temperatures until Tg was reached, at which point the specific volume decreased at a slower rate (28). Consequently the study of plasticization is a study of how to lower Tg and in doing so creating a polymer that is flexible at ambient temperature.

Today free volume is commonly defined as the difference in specific volume at some temperature of interest and some reference temperature, usually absolute zero. Free volume in the polymer can come from a variety of sources, motion of polymer end groups, motion of polymer side groups, and the internal polymer motions. Polymers will show limited motions of these types below their glass temperatures which is why unplasticised PVC is hard and rigid. These motions can be increased by raising the temperature, increasing the number of end groups, length of side chains and through the inclusion of segments of low steric hindrance and low intermolecular attractions which in turn will increase the possibility of main chain movement.

Combining these ideas with the previous theories mentioned implies that the plasticiser molecules that do not interact with the polymer chain, but simply fill free volume that is created by the molecules that do (27).

3.1.3.4 MECHANISTIC THEORY

The mechanistic theory of plasticisation can also be referred to as salvation-desolvation equilibrium and supplements the other three theories mentioned above. This theory can be seen as having some resemblance to the Gel Theory, but the essential difference is that in the mechanistic theory the plasticiser can move from one polymer location to another.

The mechanistic theory sees the association between polymer and plasticiser and between plasticiser and plasticiser as transient and ever changing. Since plasticiser molecules can migrate from plasticised polymers, it is clear that plasticiser molecules are not permanently bound to the polymer as internal plasticised resin, but that an exchange or equilibrium mechanism is present (27). At low plasticiser loadings in PVC the predominate associations are plasticiser-polymer interactions. At high plasticiser concentrations, plasticiser-plasticiser are the predominate associations (28).

3.1.4 AIMS AND OBJECTIVES

The aim of this chapter is to develop novel passive sampling materials that can be used in aquatic environments to determine TWA concentrations of pesticides in surface water. Throughout this study two prototypes were developed; one was a glass mounted passive sampler and the other was cast in a glass cylinder, removed and attached to thread so it could be suspended in water for the duration of the deployment.

This chapter outlines the steps that were undertaken in the development of this plasticised material, casting method and also looks at the enrichment profile of analytes using these novel passive sampling materials. A theoretical model is also proposed for the determination of the sampling rate of the kinetic regime.

A tuning study was undertaken with a series of plasticisers and casting methods to develop a series of passive samplers that could be selective to chemical and physical properties of target analytes.

3.2 MATERIALS AND METHODS

As in Chapter 2, atrazine and dieldrin were selected as representative analytes for the study (Table 2.1). The most commonly used plasticisers for poly vinyl chloride are certain diesters of adipic and azelate acids (30).

3.2.1 CHEMICAL REAGENTS

Pesticides (dieldrin and atrazine), fluoranthene, tetrahydrofuran (THF) , isopropyl alcohol (IPA) and PVC (average Mw approx 80,000, average Mn – 47,000) were purchased from Sigma Aldrich, Tallaght, Dublin. The plasticisers (methyl laurate, tributyl phosphate, diisononyl adipate, diisodecyl azelate) were purchased from Scientific Polymer Products Inc$^{©}$, Ontario. All of the chemicals were used without further purification. Tetrahydrofuran (THF), Methanol (HPLC grade), Isopropyl alcohol (HPLC grade) and pesticides were purchased from Sigma Aldrich (Tallaght Ireland) and were used without further processing.

3.2.2 METHODS

3.2.2.1 POLYMERIC MEMBRANES

The optimum polymeric material make up for passive sampling membranes was found to be 15% PVC (w/v), 30% diisononyl adiapte (w/w). These membranes were extracted using 1 mL of IPA for 40 min.

1 mL of polymeric material (15% PVC, 30% diisononyl adipate) was pipetted onto a microscope slide (26 x 76 mm; Breukhoven, The Netherlands). This material was then spread over the complete surface area of the microscope slide.

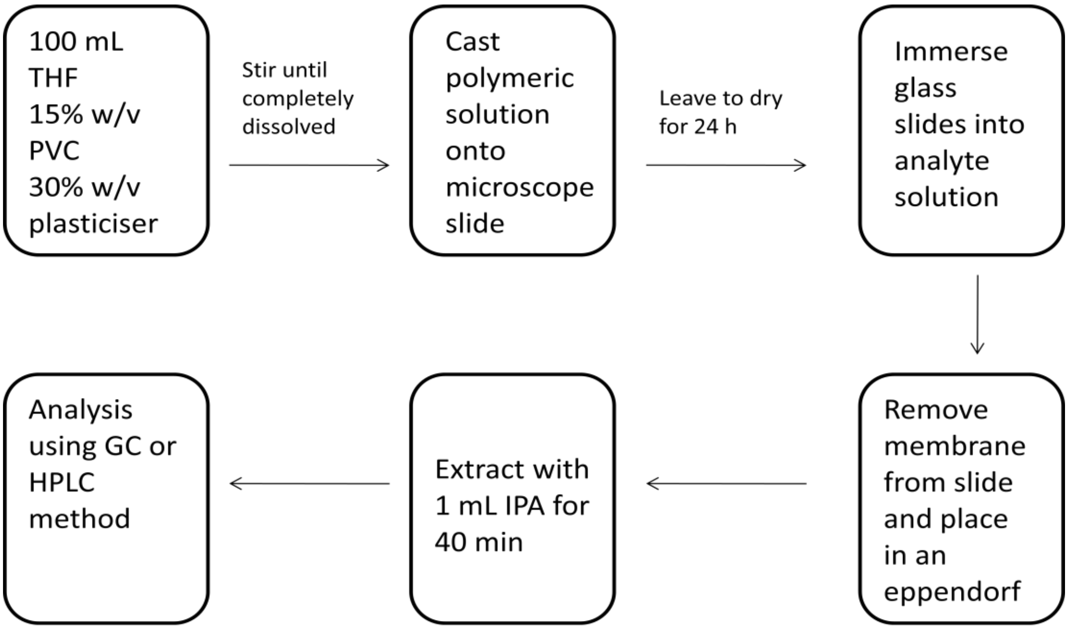


Figure 3.1: Schematic detailing steps for development and analysis of passive sampling membranes

The polymeric membranes were removed from the microscope slides using tweezers and placed in a 2 mL -centrifuge tube. 1 mL of isopropyl alcohol was added as an extraction solvent. The extraction time was 40 min, after which time the membrane was removed and the sample was ready for subsequent analysis.

3.2.2.2 POLYMERIC DISKS

The optimum polymeric material make up for passive sampling disks was found to be 15% PVC (w/v), 50% diisononyl adiapte (w/w). These membranes were cast with 3 mL of polymeric solution and extracted using 1 mL of IPA for 50 min.

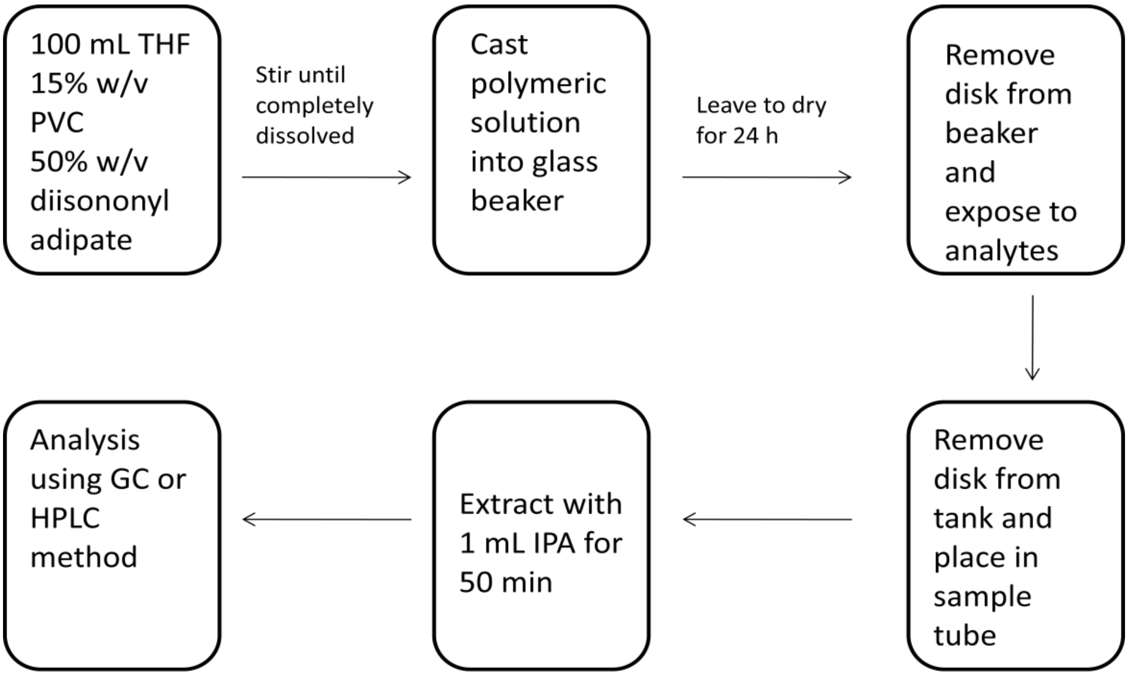


Figure 3.2: Schematic detailing steps for development and analysis of passive sampling disks

The polymeric disks were placed in a sample tube using tweezers. 1 mL of isopropyl alcohol was added as an extraction solvent. The extraction time was 50 min, after which time the disk was removed and the sample was ready for subsequent analysis.

3.2.2.1 ANALYTICAL SEPARATION

Liquid chromatographic analysis was performed with a Agilent Technologies Liquid Chromatograph (Little Island, Cork Ireland), equipped with HPLC pump (Agilent 1100 series), auto sampler (Agilent 1100 series), VWD detector (Agilent 1200 series), injection valve (Injection volume: 20 µl). The reversed phase separation was carried out using a C_{18}, 5 µm Luna column (250 mm × 4.6 mm ID, Phenomenex, CA, USA) using an isocratic binary mobile phase consisting of MeOH:Water (90:10, v/v) pumped at a flow rate of 1 mL min^{-1}, wavelength 215 nm. Both solvents were filtered through a 0.45 µm x 47 mm nylon filter (Supelco, Bellefonte, PA, USA). Separation was carried out at room temperature. The total analysis time was 8 min (as detailed in Section 2.3.3.2).

Gas chromatographic analysis was performed with a HP 6890 series gas chromatograph connected to HP 5973 mass-selective detector was employed. The gas chromatograph was equipped with an Agilent 7683 auto sampler and split/splitless injector with electronic pressure control. An Agilent HP5-MS ((5%-Phenyl)-methylpolysiloxane) fused silica capillary column 30 m × 0.25 mm ID × 0.25 µm (film thickness) was used, with helium (99.99%) as carrier gas at a constant flow of 1.1 mL min^{-1}. The temperature programme was the following: initial temperature 40 °C, held for 2 min, 9 °C·min^{-1} ramp to 170 °C, 3 °C min^{-1} to 205 °C, then 1 °C min^{-1} to 208 °C finally by 20 °C min^{-1} to 290 °C and held for 13 min. The total analysis time was 36.42 min and the equilibration time 6 min. The temperature of the injection port was 250 °C and a 20 µL volume was injected in splitless mode.

The mass spectrometer was operated in electron ionisation mode with an ionising energy of 70 eV, ion source temperature 230 °C, MS Quad temperature 150 °C, electron multiplier voltage (EMVolts) 1750 V when performing selected ion monitoring, scanning from m/z 50 to 400 at 3.25 s per scan; solvent delay, 8.5 min (as detailed in Section 2.3.2.4).

3.2.2.2 SAMPLE PREPARATION

Concentrations of 1 and 0.1 mg L^{-1} of atrazine and dieldrin were prepared. For initial screening studies polymeric membranes (Section 3.2.2.1) were immersed in the 1 mgL^{-1} solution for a period of 24 h and extracted for a period of 48 h.

The testing process involved spiking a tank of water with a known concentration e.g. 1 mgL^{-1} of the priority pollutant e.g. atrazine. The polymer membranes and disks (Section 3.2.2.2) were placed in the tank for selected times (samples taken on a regular basis generally 0.5-1 h) and then extracted (Section 3.313 & 3.3.2.2 for polymeric disks and membranes respectively) and analysed using HPLC (Section 2.3.3) or GC methods (Section 2.3.2).

3.3 RESULTS AND DISCUSSION

3.3.1 PROTOTYPE 1: GLASS MOUNTED POLYMER THIN FILMS

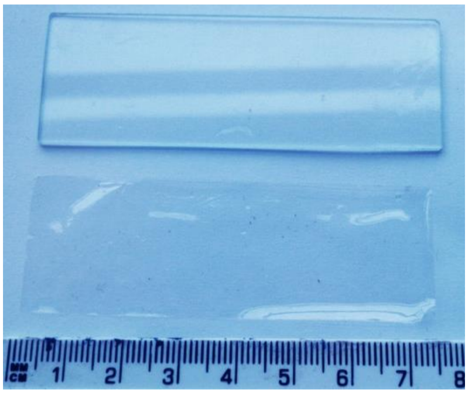


Figure 3.3: Passive sampling membranes (Prototype 1). Passive sampling membranes cast on glass slide pre exposure (above); Passive sampling membrane removed from slide post exposure for extraction (below)

For the purposes of optimization of this prototype all studies within this section were carried out with two target analytes; atrazine and dieldrin. These analytes have been previously mentioned in Chapter two with detailed physical and chemical characteristics (Table 2.1) and were chosen to encompass the wide range of pesticides to be monitored

3.3.1.1 CASTING OF GLASS MOUNTED POLYMER THIN FILMS

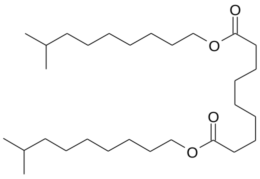
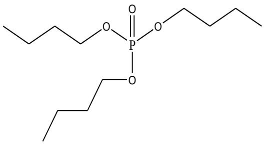
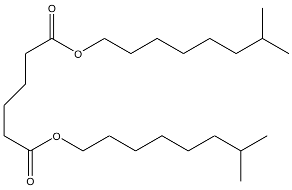
The materials were prepared by dissolving the PVC in 100 mL THF, with the specific plasticiser added. The polymeric solution was then thoroughly mixed and cast onto a clean glass slide. Polymeric material (1 mL) was pipetted onto a microscope slide (26 x 76 mm; Breukhoven, The Netherlands). This material was then spread over the complete surface area of the microscope slide. The polymeric solution was allowed sufficient time to dry under normal laboratory conditions.

3.3.1.2 OPTIMIZATION OF PLASTICISED MEMBRANE

A selection of plasticised membranes were made up consisting of PVC and a specific plasticiser in THF. The plasticisers encompassed three plasticisers groups: Adipates, Azelates, and Phosphates. From these groups, diisononyl adipate, diisodecyl azelate, and tributyl phosphate were selected and chemical and physical properties are outlined below (Table 3.1).

All passive sampling membranes were made up with 5% polymer (PVC) (w/v) and 30% plasticiser (varied plasticiser type outlined in Table 3.1), with the exception of one passive sampling membrane with contained no plasticiser (5% PVC). These membranes were immersed in a 1 mgL^{-1} solution of atrazine and dieldrin for a period of 24 h, and extracted using a selection of four solvents; isopropyl alcohol, acetonitrile, hexane and methanol, over a period of 48 h. These extracts were then analysed using GC-MS as outlined previously (Section 2.3.2.4) to determine which plasticised membrane showed the highest enrichment of the two target analytes

Table 3.1: Overview of plasticisers used in this study. Selected physical and chemical properties of three plasticisers used within study of enrichment rates for atrazine and dieldrin.

	Diisodecyl Azelate	Tributyl Phosphate	Diisononyl adipate
Structure			
Molecular Formula	$C_{29}H_{56}O_4$	$C_{12}H_{27}O_4P$	$C_{24}H_{46}O_4$
Molecular Weight (gmol^{-1})	468.75	266.36	398.62
Density (gcm^{-3})	0.91	0.98	0.92
Log K_{ow}	11.45	4.27	9.16

It was found from the study of extraction solvent that there was enrichment of analytes into all four membrane types. Out of the four passive sampling membranes tested the best performing for atrazine were diisononyl adipate, showing the greatest enrichment and extraction with acetonitrile. For the purpose of this the best plasticiser/ solvent combination was considered as 100% enrichment and the remained results would be calculated in relation to this for ease of viewing as the pre concentration effects of the membrane were removed (Table 3.2).

The unplasticised membrane (5% PVC) showed a greatly decreased enrichment of atrazine. The greatest extraction was seen with diisononyl adipate extracted with acetonitile with 0.82 mgL^{-1} followed closely by diisononyl adipate with 0.81 mgL^{-1}. The worst performing membrane in terms of enrichment of analytes was seen to be the unplasticised membrane (5% PVC) showed a greatly decreased enrichment of atrazine, 0.08 – 0.0004 mgL^{-1} with the selection of extraction solvents (Table 3.2). It can be seen with the polar nature of atrazine, that the unplasticised PVC alone did not share the affinity needed to aid enrichment of the analyte. Increased enrichment was found for atrazine when plasticiser is introduced into the polymeric solution as the chemical and physical properties of the polymeric solution were altered and then shared a greater affinity with the polar target analytes.

Table 3.2: Percentage recoveries for atrazine (top) and dieldrin (bottom) for plasticised membranes after exposure to 1 mgL^{-1} for 24 h and extracted for 48 h with selected solvents prior to analysis on the GC-MS. Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min)

Atrazine				
	Tributyl phosphate	*Diisononyl adiapte*	*Diisodecyl azelate*	*Unplasticised*
Acetonitrile	28.39	100.00	25.35	10.88
Methanol	0.05	20.89	61.02	0.31
Isopropyl alcohol	76.45	98.51	73.89	19.02
Hexane	21.82	7.94	9.67	0.37
Dieldrin				
	Tributyl phosphate	*Diisononyl adiapte*	*Diisodecyl azelate*	*Unplasticised*
Acetonitrile	77.52	68.70	51.18	49.12
Methanol	57.19	33.92	53.24	50.33
Isopropyl alcohol	100.00	94.70	62.01	64.91
Hexane	9.86	28.29	8.71	9.38

As can be seen dieldrin showed enrichment into all four passive sampling membranes also (Table 3.2). The best performing membrane for the enrichment of dieldrin was seen to be tributyl phosphate when extracted with acetonitrile. The unplasticised membrane showed greater enrichment results with dieldrin in comparison to atrazine showing an enrichment of 9.4-64.9% in comparison to 0.3-19.02%. The non polar properties of dieldrin can be seen with respect to the enrichment of dieldrin in the unplasticised membrane. It can be seen that while there is an increase in the analyte uptake when plasticiser is added to the polymeric solution, in the case of dieldrin this increase is not as significant. In comparison with the results found with atrazine where a significant increase in analyte enrichment was noted. Of the four membranes tested tributyl phosphate showed the greatest affinity with dieldrin.

It should be noted that while unplasticised PVC showed acceptable enrichment of dieldrin, that the membrane was rigid and was not believed to be robust enough to have survived exposure as a long term sampler in environmental studies. This was due to the fact that with longer exposure times (> 7 days) the material started to 'crack'.

It can be seen that these polymeric membranes show uptake of the target analytes and can be extracted and analysed using methods described in Chapter 2. However, the plasticized membranes studied were at 15% w/v PVC so a further study was carried out to determine the effect that percentage w/v of PVC had on the uptake and extraction of these analytes. Two plasticised membranes and two solvents were selected for this study based on the results from the previous study (Table 2). Tributyl phosphate and diisononyl adipate had shown an affinity for dieldrin and atrazine. As can be seen in both cases isopropyl alcohol and acetonitrile gave the best results for both atrazine and dieldrin. These two solvents were the selected for a further study to investigate the affect of percentage (w/v) of PVC in the membrane on the uptake rate of analytes.

While determining the optimum percentage of PVC in the thin film, three different variations were tested. The percentages (w/v) of PVC in the membranesstudied were 5, 10 and 15% with the percentage plasticiser remaining constant (30% (w/w)). Attention should be drawn to the fact that within the results below the percentage of polymer is only shown up to 15%. A 20% PVC solution was prepared however this polymeric solution was deemed too viscous for casting of uniform membranes.

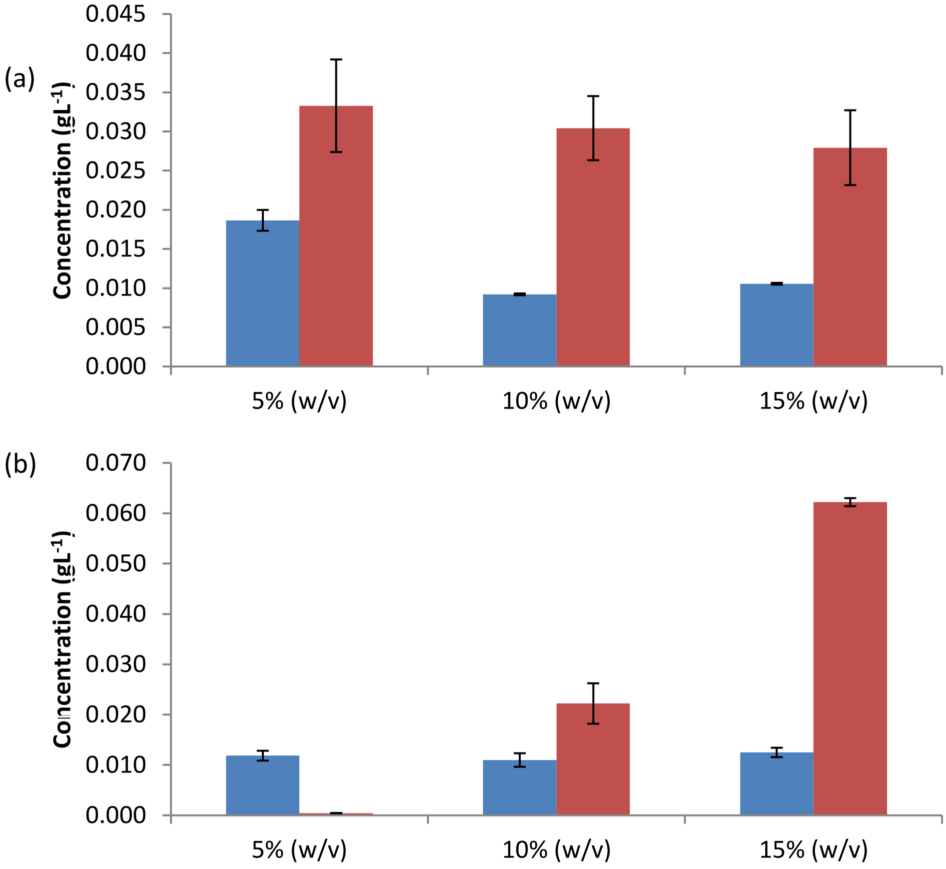


Figure 3.4: Overview of results for varied percentage polymer (w/v) extracted with acetonitrile. This figure shows two plasticisers (tributyl phosphate (a), diisononyl adipate (b)) (30% w/w) when extracted with acetonitrile for 48 h after 24 h exposure to 1 mgL^{-1} (Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min))

For the polymer containing tributyl phosphate results show that the concentration of atrazine decreases with increasing percentage of PVC (Figure 3.4 (a)). This can be attributed to the leaching of tributyl phosphate which was observed when looking at the GC-MS chromatograph obtained for the samples. This leaching of plasticiser will affect the enrichment of atrazine more so that of dieldrin due to the hydrophilic nature of the compound as seen previously (Table 3.2). It was also shown with the diisononyl adipate results (Figure 3.4 (b)) as the percentage of PVC increased so too did the enrichment of the pollutants.

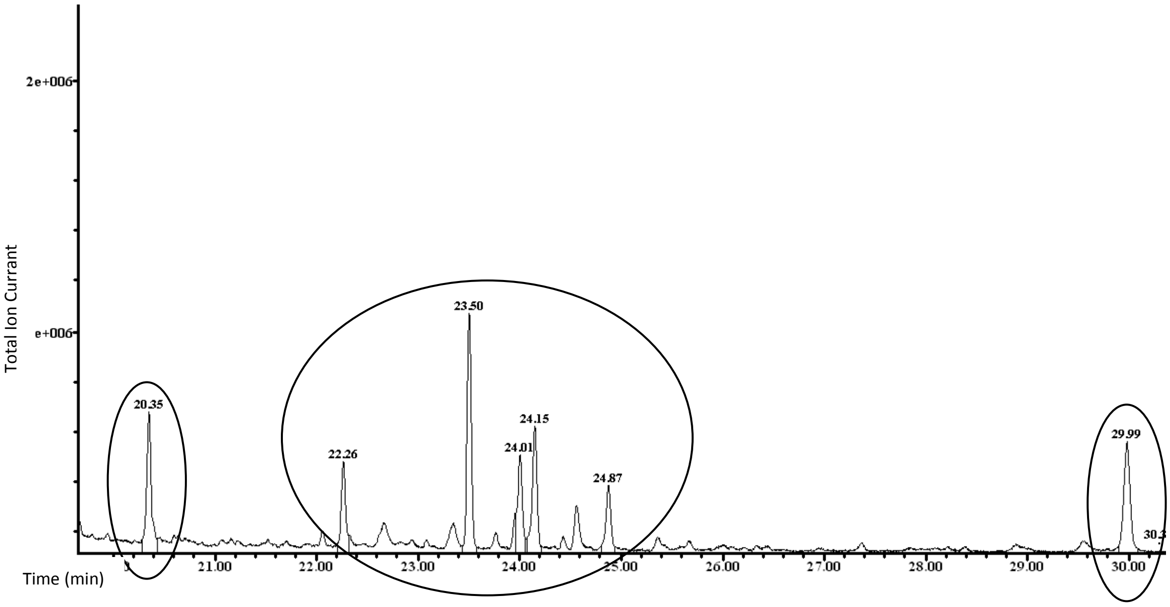


Figure 3.5: GC Chromatogram of passive sampling membrane (5% PVC (w/v), 30% tributyl phosphate (w/w). The membrane was exposed for 24 h to a solution containing 1 mgL^{-1} of atrazine (circled left) and dieldrin (circled right) after 48 h extraction with IPA. Tributyl phosphate and degradation products are also seen (circled centre) (Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min)

The chromatogram above shows both analytes; atrazine (20.35 min) eluted before dieldrin (29.99 min) (Figure 3.5). It can also be seen that there was a selection of analyte peaks that appeared between these two target peaks which were identified as tributyl phosphate (23.50 min) and a degradation product, dimethyl methyl phosphate (22.26 min) using mass spectra software (Library: NIST98). This shows that this passive sampling membrane design would not be suitable both for enrichment of analytes or for environmental exposure. Due to the leaching of the plasticiser, both the sensitivity of enrichment and also the rigidity of the membrane will be affected.

When the polymer membranes doped with tributyl phosphate (Figure 3.6 (a)) were extracted with isopropyl alcohol the same trend that was noted with acetonitrile was observed; as the percentage of PVC increased the enrichment concentration of the pollutants decreased. With the polymer membranes containing diisononyl adipate the opposite trend was observed (Figure 3.6 (b)). It was found that as the percentage of the PVC was increased so too did the enrichment of both analytes. For dieldrin a 52% increase in concentration was observed as the percentage of PVC was increased from 5% to 15%. This shows that while dieldrin has an affinity for PVC this factor alone is not sufficient for satisfactory enrichment. As the plasticiser was removed (via leaching) the enrichment of dieldrin did decrease by17%.

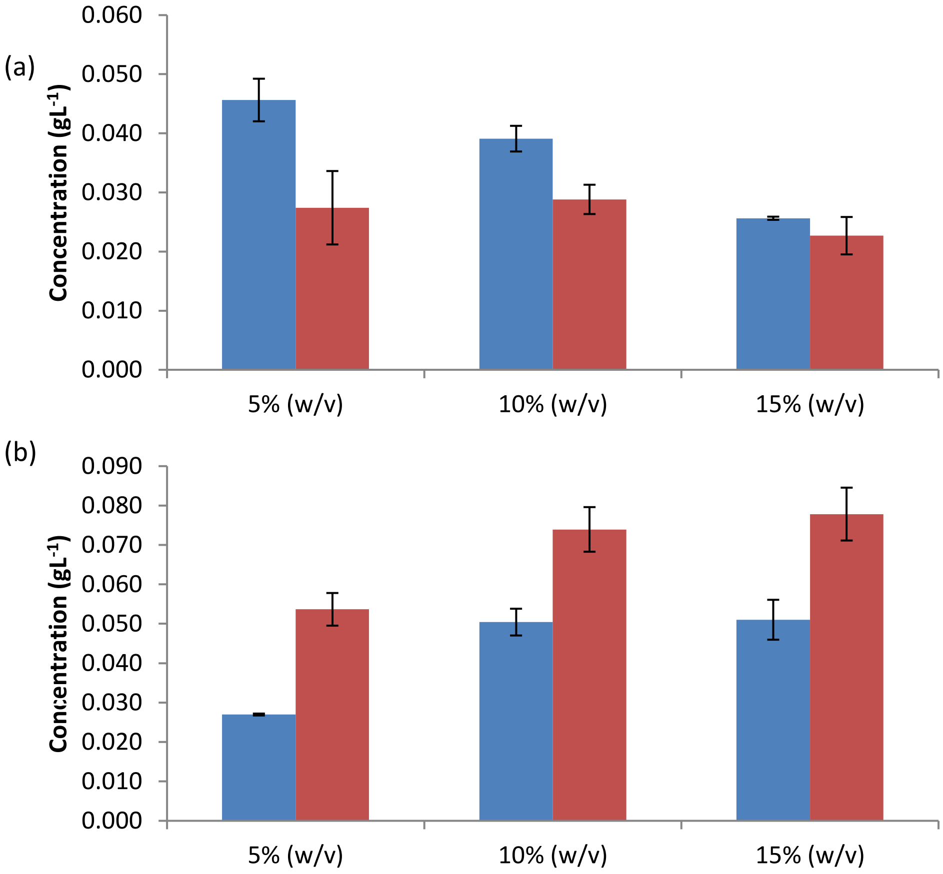


Figure 3.6: Overview of results for varied percentage polymer (w/v) extracted with isopropyl alcohol. This figure shows two plasticisers (tributyl phosphate (a), diisononyl adipate (b)) (30% w/w) when extracted with isopropyl alcohol for 48 h after 24 h exposure to 1mgL^{-1} of atrazine and dieldrin. Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min)

It can be deduced from this that the favoured plasticiser to encompass the range of pesticides within the study was diisononyl adipate (15% PVC (w/v)), which showed the highest enrichment concentrations of atrazine and dieldrin. For the extraction solvents, while both solvents showed similar trends, isopropyl alcohol showed greater extraction of the target analytes most notably for atrazine.

In each case it was seen that isopropyl alcohol was the optimum solvent, showing a higher extraction of both the target analytes. As can be seen above with both solvents diisononyl adipate showed higher concentrations of both analytes, showing this make up of polymeric membrane to be the optimum (Figure 3.4 & Figure 3.6). Higher percentages (w/v) of PVC were not tested as the resulting polymeric solutions were deemed too viscous for the making of reproducible films. For the tributyl phosphate passive sampling membranes, as the percentage of PVC (w/v) increased the concentration of the analyte decreased. The uptake rate was compromised due to leaching occurring of the tributyl phosphate plasticiser, which was seen alongside degradation of the plasticiser using the mass spectrum obtained and was seen with both solvents. The highest concentrations of both analytes can be seen with the 15% diisononyl adipate using isopropyl alcohol as an extraction solvent. After this had been determined it was deemed necessary to decrease the extraction time from 48 h to a less time consuming method if possible.

3.3.1.3 OPTIMISATION OF EXTRACTION TIME

As previous studies had been carried out with a long extraction time (48 h) a study was undertaken to determine if this time could be shortened (Section 3.3.1.2). In doing so it was hoped to make the method more time effective. Passive sampling membranes (15% PVC (w/v), 30% (w/w) diisononyl adipate) were exposed to tanks containing 1 mgL^{-1} of atrazine and dieldrin for a period of 24 h to ensure that adequate enrichment of analytes was obtained. These passive sampling membranes were then extracted with 1 mL of isopropyl alcohol for selected time periods ranging for 10 min to 80 min.

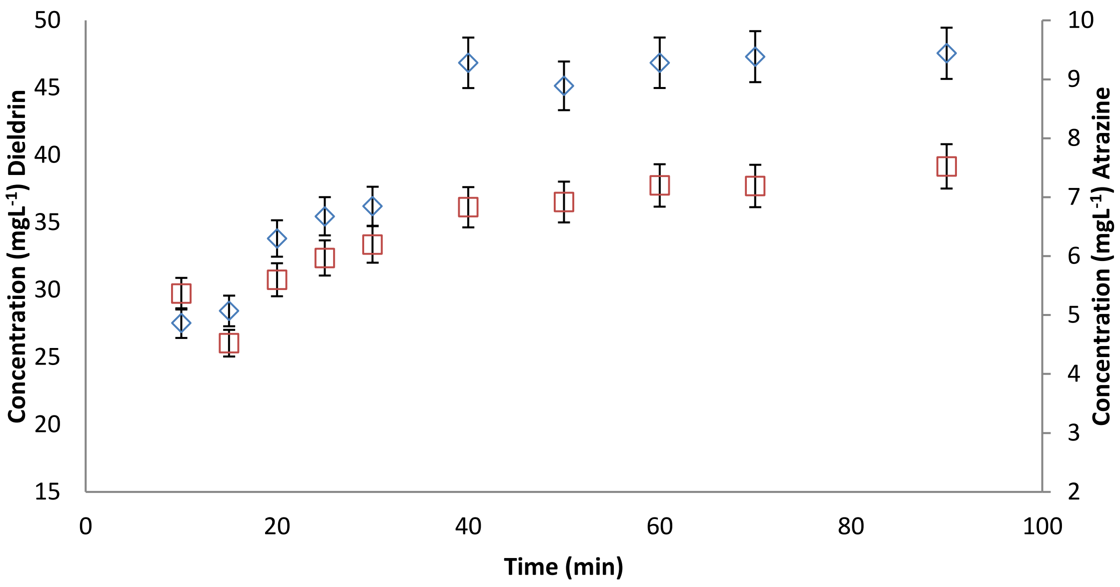


Figure 3.7: Determination of optimum extraction time. The passive sampling membranes were exposed to 1 mgL^{-1} of atrazine (blue) and dieldrin (red) for a period of 24 h and extracted over a series of time points with isopropyl alcohol (n=3) The samples were analysed using a C18 (250 mm x 4.6 mm ID 5 µm Luna column, mobile phase 95:5 v/v acetonitrile:water.

An extraction curve for the two target analytes using isopropyl alcohol is shown above (Figure 3.7). The disks were all removed from a tank spiked with 1 mgL^{-1} of atrazine and dieldrin at the same time. The disks were then extracted for a selection of different times (increments of 10 min). This study was carried out in triplicate for each of the time points. As can be seen at the 40 min time mark both of the target analytes have levelled off to a plateau showing that this is the optimum extraction time for these passive sampling devices with this range of target analytes.

3.3.1.4 ENRICHMENT OF PESTICIDES

The glass mounted passive sampling thin film was developed and optimized with an extraction method detailed above (Section 3.3.3). A study was carried out to look at the enrichment rates of target analytes into the glass mounted passive sampling thin films at varied concentrations. The first study carried out was at a concentration of 1 mgL^{-1} and is detailed below (Figure 3.8).

Passive sampling membranes were immersed in a tank spiked with 1 mg L^{-1} of both atrazine and dieldrin, with samples being taken at intervals over a period of 8 d with more regular samples been taken for the first 6 h to determine if a lag phase was noted.

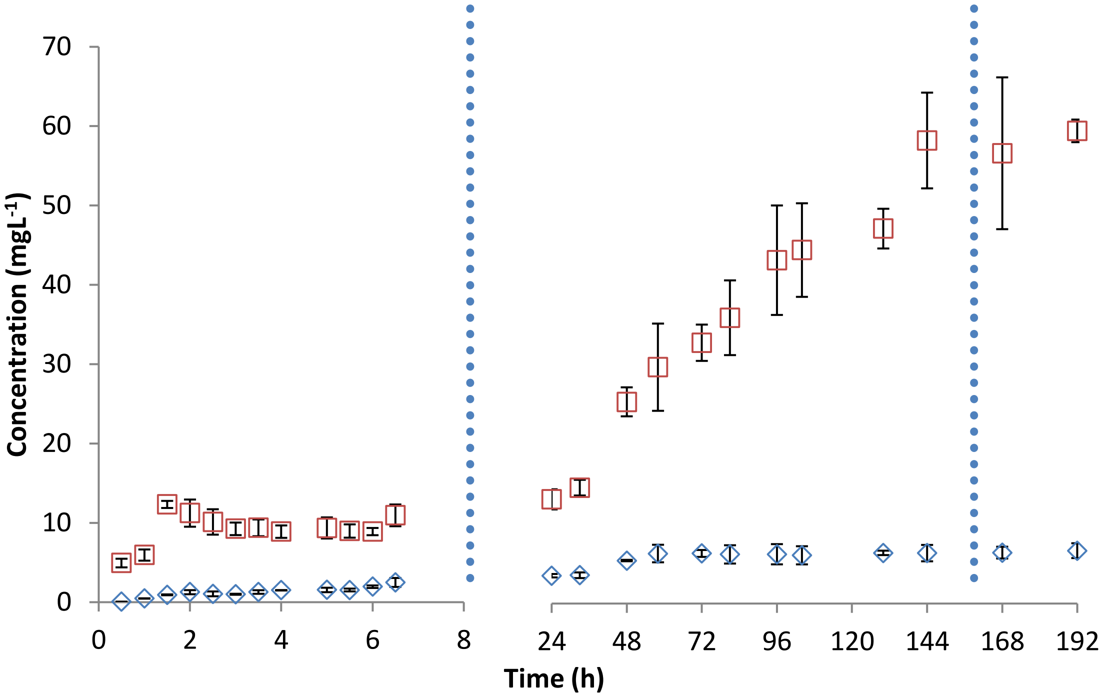


Figure 3.8: Enrichment of analytes at 1 mgL^{-1}. Enrichment of atrazine (◊) and dieldrin ([]) with slope shown inset (n=3) broken down into the three distinct areas; initially a lag phase is seen, followed by the kinetic regime, and finally an equilibrium phase. The samples were analysed using a C18 (250 mm x 4.6 mm ID 5 µm Luna column, mobile phase 95:5 v/v acetonitrile:water.

Two diffusion curves can be seen above for both atrazine and dieldrin at 1 mgL^{-1} (Figure 3.8), these curves can be broken down into three distinct regions. Initially the passive sampling membranes experience a lag phase, in this case this lasted 6.5 h for dieldrin and 6.0 h for atrazine. Following the lag phase a kinetic regime was entered by the target analytes. During this time a linear regression can be seen for both compounds; dieldrin (slope = 0.3402, intercept = -7.0775) and atrazine (slope = 0.0262, intercept = 2.3449). After the kinetic regime a phase of equilibrium was reached by both compounds which for atrazine happened at 130 h whereas dieldrin took longer at 144 h.

When looking at the concentration of the analytes at equilibrium a pre concentration into the membrane can be seen. Atrazine reached equilibrium with a concentration of 5.2 mgL^{-1} whereas the equilibrium concentration of dieldrin was seen to be higher at 57.2 mgL^{-1}. As illustrated above both analytes reached equilibrium(Figure 3.8), however attention should be drawn to the different rates at which both analytes reached equilibrium. Atrazine shows a quicker enrichment into the passive sampling membrane than dieldrin, almost 11.5 times faster and reaches equilibrium at an earlier time. However, while dieldrin has a slower enrichment rate than atrazine a higher concentration of analyte was extracted from the membranes exposed to dieldrin.

The atrazine shows an affinity for diisononyl adipate as observed from previous results (Section 3.3.1.2). As the membrane has a large surface area, with exposed diisononyl adipate molecules, the atrazine enriches at a greater rate than dieldrin. However the membrane is still more hydrophobic than hydrophilic and therefore we see a higher equilibrium concentration of dieldrin.

Passive sampling membranes were immersed in a tank spiked with 0.1 mg L^{-1} of both atrazine and dieldrin, with samples being taken at twelve hour intervals over a period of 8 d.

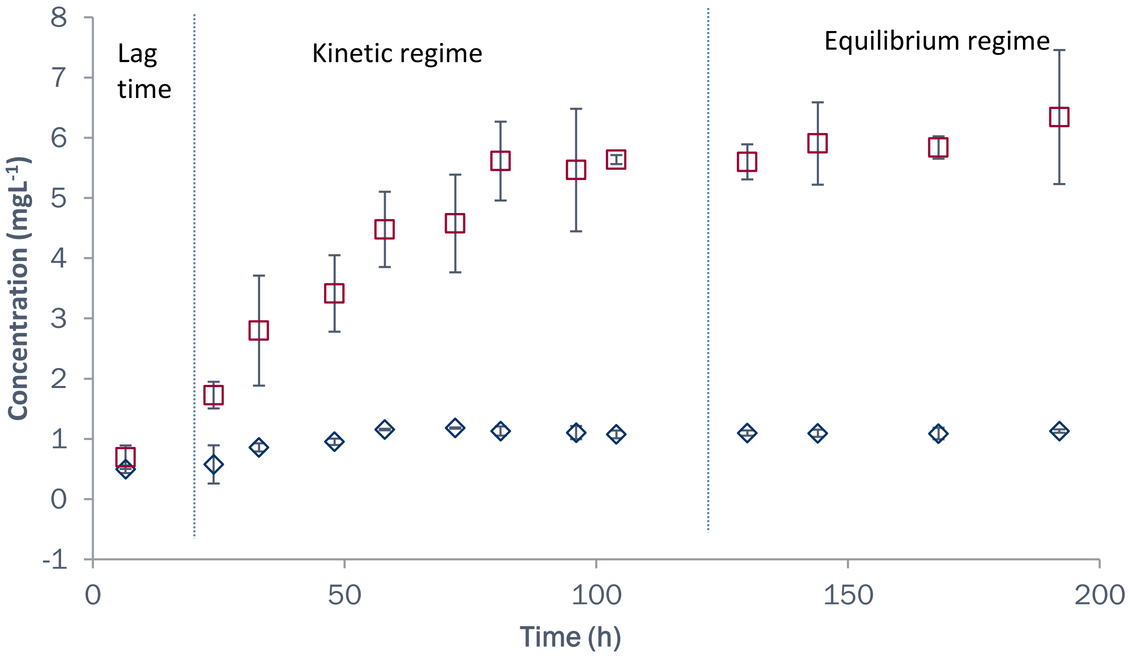


Figure 3.9:Enrichment of analytes at 0.1 mgL^{-1} into glass mounted polymer membranes. Enrichment of atrazine (◊) and dieldrin ([]) into plasticised membranes (15% w/v PVC, 30% w/w diisononyl adipate) (n=3) The samples were analysed using a C18 (250 mm x 4.6 mm ID 5 µm Luna column, mobile phase 95:5 v/v acetonitrile:water.

As can be seen in Figure 3.9, initially the passive sampling membranes experience a lag phase, in this case this lasted 6.5 h for dieldrin and 6.0 h for atrazine. Following the lag phase a kinetic regime is entered. During this time a linear regression can be seen for both compounds; dieldrin (slope = 0.0598, intercept = 0.6237) and atrazine (slope = 0.0048, intercept = 0.0519). After the kinetic regime a phase of equilibrium was reached by both compounds, which for dieldrin occurred at 80 h whereas atrazine was longer at 144 h. When looking at the concentration of the analytes at equilibrium a pre concentration into the membrane can be seen. Atrazine reached equilibrium with a concentration of 0.75 mgL^{-1} whereas the equilibrium concentration of dieldrin was seen to be higher at 5.6 mgL^{-1}.

The glass mounted passive sampling disks show promise, however, there were several issues with this prototype. Initially the material was cast onto a glass support slide in the hope that the novel polymeric membrane could be analysed both using ATR either as a substitute or prior to extraction and analysis using HPLC or GC. This was found problematic, whilst the membrane could be analysed using ATR, there were several issues ensuring that the film was uniformly mounted on the ZnSe crystal, and also issues with the sensitivity of this technique.

Another issue that was noted with the glass mounted polymer membranes was in relation to the deployment. These slides could be placed into the tank or using slide holders. Whilst this deployment worked within the laboratory environment it was not deemed robust or viable for environmental deployment.

One other issue that was observed was with the membranes was thatduring short deployment times they remained adhered to the glass slides, however when the deployment time was increased (seven days or over) the films started detaching from the glass slides. This was a large issue for longer deployments as it increased the surface area available for enrichment of analytes. For longer deployments it was necessary to use glass slide holders that not only supported the glass mounted membranes, but also aided in maintaining the membranes in place. For these reasons mentioned a second prototype of sampler was developed that was considered to be more robust and desirable for environmental deployment.

3.3.2 PROTOTYPE 2: PASSIVE SAMPLING DISKS

Figure 3.10: Novel Passive sampling disk. Passive sampling membranes cast from glass cylinder pre exposure (left) (21 mm * 0.2 mm); 20 cent coin for size comparison (ri-ght)

This prototype was developed using the data determined from the optimisation studies mentioned in the above section (Section 3.3.1)

As with the previous prototype development of this sampler was initially tested using atrazine and dieldrin used to encompass the group of pesticides.

It was significant to have passive sampling devices which not only showed enrichment of the target analytes, as seen with the passive sampling membranes (Section 3.3.1), but that also were robust enough to survive environmental conditions which they would be exposed to. For this reason the other methods of casting the polymers were investigated. One way that showed great promise was casting of a passive sampling disk (Figure 3.10).

3.3.2.1 CASTING OF NOVEL PASSIVE SAMPLING DISKS

A 10 mL beaker was selected for initial tests, and various volumes (1,3,8 mL) of the polymeric solution were cast to determine the optimum volume for the passive sampling disks.

When 1 mL of polymeric solution was introduced a flat disk was developed. This volume dried rapidly, however when the disk was removed from the cast it was very flexible and not robust. Next 3 mL of polymeric solution was added, and while the drying time was now increased to approx 12 h with air drying, a flat uniform disk was obtained. This disk was considered robust enough to survive aquatic conditions. Following on from this 8 mL was introduced into the cast to determine if it was possible to create a disk that was more robust than the 3 mL disk with greater bulk volume. However this was not found to be the case. This disk took the longest to dry (approx 24 h air drying) and once dry it was noted that the resulting disk was hollow in the centre. This was not suitable as there was now air trapped within the disk. The 3 mL disk was used for further studies; the first of which was to determine if it was possible to reduce the drying time of the disks. While testing the volumes of the disks air drying in standard laboratory conditions was carried out.

Three new methods for drying were tested, these included: vacuum and oven drying, air drying and using a desiccator. The vacuum oven drying was tested at 100 psi, 300 psi and 760 psi. The 100 psi pellet gave a flat but not rough surface which contained air bubbles. The 300 psi pellet did not flatten completely and also contained some air bubbles. The 760 psi pellet did not result as a flat pellet and also contained many air bubbles.

Another selection of disks were left in a desiccator overnight to dry. While these disks gave a good uniform shape with minimal air bubbles present this method took a longer time than the current method in use (air drying). The 1 mL disk nearly fully evaporated leaving only a slight layer of polymeric material left. This was unsuitable, as a thicker disk had been determined to be more suitable and robust for the detection of pesticides in water. The 3 mL disk gave a nice flat shape with ridges up the sides but contained some air bubbles within the disk. The 8 mL disk ended up being very thick, and while this may be more robust for environmental exposure it should be noted that similar to the 8 mL results mentioned above the disk dried hollow. It was found that air drying gave the optimum shape as the disk totally flattened out leaving only ridges on the side of the 10 mL beaker which could be removed; also there were no air bubbles found. From these results it was concluded that the air drying method was the optimum drying method. It left the disks being totally flat with no air bubbles and was also a quick drying method.

3.3.2.2 OPTIMISATION OF EXTRACTION TIME

Due to the bulk increase and thickness of the sampler the extraction time was investigated again to ensure that the analytes were fully extracted from the disks. The samplers were exposed to 1 mgL^{-1} of atrazine and dieldrin for a period of 24 h and extracted with 1 mL of IPA over a series of time points. A similar extraction profile was seen for the passive sampling disk as shown for passive sampling membrane (Figure 3.7). However a longer extraction time, 50 min was necessary to extract the target analytes from the disks. This can be attributed to the difference in thickness between the passive sampling membranes and passive sampling disks.

3.3.3.3 OPTIMISATION OF PERCENTAGE PLASTICISER

As mentioned above the 15% (w/v) PVC polymeric solution that was determined in the previous section was used for these initial studies. During these previous studies the percentage of plasticiser was maintained at a constant 30% (w/w). For the purposes of extending the sensitivity of the passive sampling disk a short study was undertaken to ensure that the optimum volume of plasticiser was introduced into the polymeric solution.

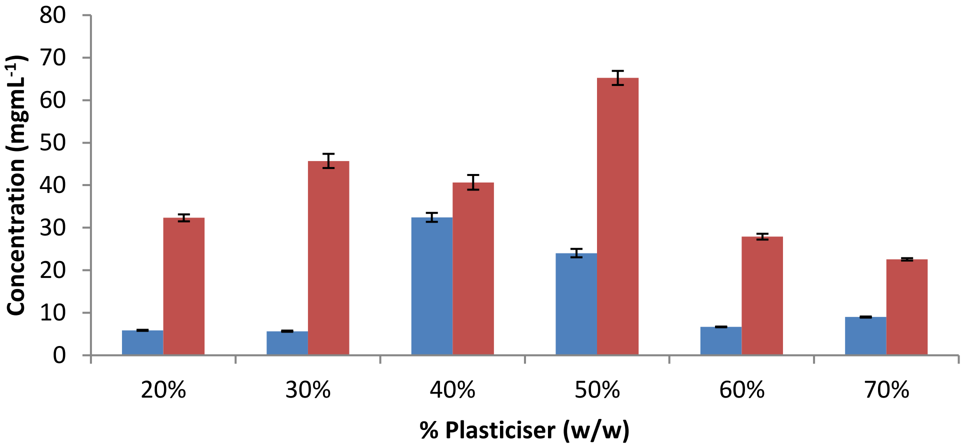


Figure 3.11: Determination of optimum percentage plasticiser (w/w). Results showing analyte concentration in six separate PS disks (15% w/v PVC) with varying percentage of diisononyl adipate after exposure to atrazine (blue) and dieldrin (red) for 48 h and extraction in isopropyl alcohol for 50 min. (n=3). The samples were analysed using a C18 (250 mm x 4.6 mm ID 5 µm Luna column, mobile phase 95:5 v/v acetonitrile:water.

The passive sampling disks were immersed in solutions containing 1 mgL^{-1} of atrazine and dieldrin for a period of 24 h and extracted using IPA (1 mL) for 50 min. It can be seen that there is a more noticeable increase in concentration of atrazine with increased plasticiser up to 40% (Figure 3.11), which is due to the affinity of atrazine for diisononyl adipate as mentioned earlier (Section 3.3.1.2).

A 50% plasticiser (w/w) composition was selected for the passive sampling disks. This polymeric make up showed the best enrichment of dieldrin, but the concentration of atrazine had been slightly reduced. The reason that the 40% plasticiser make up was not selected was due to the rigidity of the passive sampling disks obtained. When these disks were left in solution for long periods of time (1 week and upward) the surface started to 'crack'. Due to this they were not deemed fit for aquatic environmental exposure. As the plasticiser percentage increased (60-70%) the disks became more and more flexible and also were not considered robust enough for deployment.

3.3.3.4 ENRICHMENT OF PESTICIDES

A study was carried out to look at the enrichment rates of target analytes into the novel passive sampling disks at varied concentrations. The first study carried out was at a concentration of 1 mgL^{-1} and is detailed below (Figure 3.12).Passive sampling materials were immersed in a tank spiked with 1 mg L^{-1} of both atrazine and dieldrin, with samples being taken at intervals over a period of 12 h.

As seen from previous studies both analytes reached equilibrium (Section 3.3.1.4), but as with the passive sampling membranes there is a significant difference in the uptake rate of both target analytes. This would be expected due to the polarity of the plasticiser selected which has a Log K_{ow} of 9.16, this matches more closely to the Log K_{ow} of dieldrin (5.4). In the case of these passive sampling disks it is seen that dieldrin shows the increased enrichment rate in comparison to atrazine, with a three fold increase.

When the polymer bulk was increased a decrease in exposure time was observed. Equilibrium was reached within 6 h for the passive sampling disks whereas a much longer period of time was needed for the passive sampling membranes (5.5 days). As well as a shorter sampling time the passive sampling disks showed a greater pre-concentration factor for atrazine, with an equilibrium concentration of 15 mgL^{-1}, in comparison to 6 mgL^{-1} that had been seen in the passive sampling membranes. This shows a 2.5 fold increase in concentration between the disks and the membranes. This trend was also noted for dieldrin however, the increase in concentration was not a great as with atrazine, 65 mgL^{-1} in disks compared to 55 mgL^{-1} in membranes. This shows a 1.2 fold increase in concentration between the disks and the membranes.

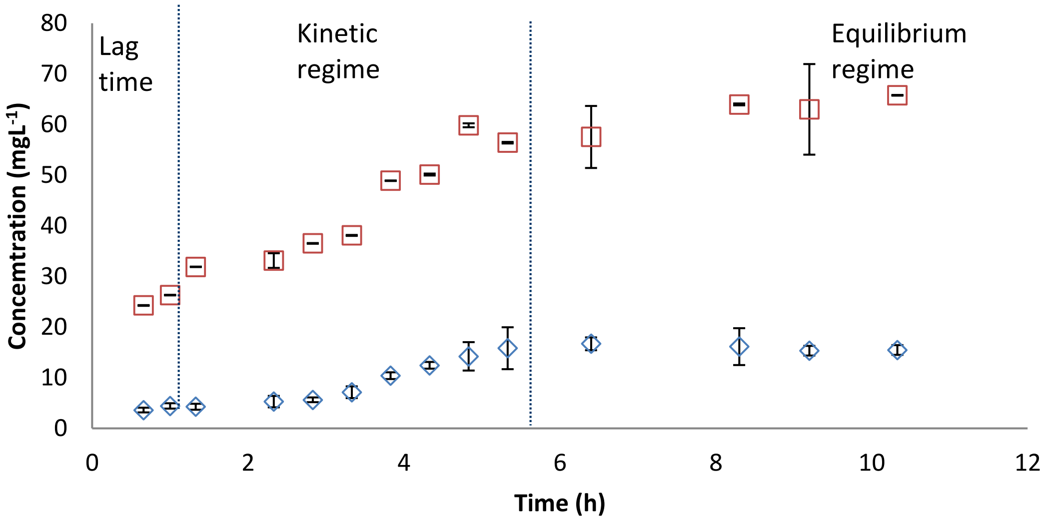


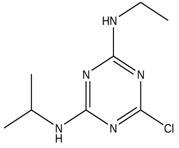
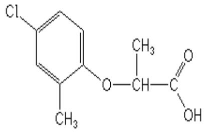
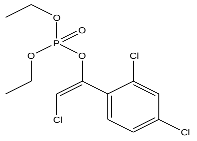
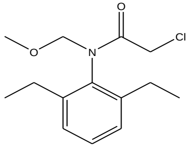
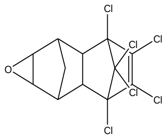
Figure 3.12: Diffusion profile of two analytes at 1 mgL^{-1} into passive sampling disks: Results showing analyte diffusion into PS disks (15% w/v PVC, 50% w/w diisononyl adipate) for target analytes over time (atrazine (blue) and dieldrin (red)) extracted with isopropyl alcohol for 50 min (n=3). The samples were analysed using a C18 (250 mm x 4.6 mm ID 5 µm Luna column, mobile phase 95:5 v/v acetonitrile:water.

Not only was a higher equilibrium concentration noted, there was a large increase in the slope of the kinetic regime with the passive sampling disks in comparison to passive sampling membranes. As seen in previous enrichment curves (Figure 3.8) there were three distinct regimes. Firstly a lag phase is noted which was seen to be much shorter than with passive sampling membranes, 1 h for atrazine and 40 min with dieldrin. Subsequent to the lag phase is a kinetic regime, where a linear regression can be seen for both of the analytes; dieldrin (slope = 5.7361, intercept = 22.651) and atrazine (slope = 2.5688, intercept = 0.6352) After this an equilibrium range was entered by both compounds (6.4 h for atrazine and 8.3 h dieldrin)

3.3.3 MODEL FOR THE PREDICTION OF KINETIC SAMPLING RATE

For the development of the prediction model for kinetic sampling rates, initially five distinct pesticides were selected. Their molecular structures, and selected chemical and physical properties are outlined below (Table 3.3). The enrichment profiles of these pollutants were studied at a concentration of 0.1 mgL^{-1} for each analyte individually. From these profiles the main area of study was based on the kinetic rate calculated. The kinetic rate was calculated and plotted against the compounds Log K_{ow} to determine if a correlation between the rate values and Log K_{ow} could be determined (Figure 3.13).

Table 3.3: Selected properties of analytes used for prediction model.

	Atrazine	Mecoprop	Chlorfenvinphos	Alachlor	Endrin
					
Density	1.269	1.265	1.373	1.12	1.84
Log K_{ow}	2.6	2.8	3.8	3.5	5.2
Mol. Weight ($gmol^{-1}$)	215.68	214.65	359.57	269.77	380.91

To calculate the rate constant of the kinetic regime was calculated using Equation 1.3 mentioned in Chapter 1 previously. This equation works on the assumption that the mass transfer of analyte from the aqueous environment is linearly proportional to time.

$$C_s(t) = C_w k_1 t \qquad \text{(Eqn. 3.1)}$$

Where $C_s(t)$ is the concentration in the sampler at time t, C_w is the concentration in the aqueous environment, k_1 is the first order rate constant for pollutant uptake and t is the sample time. To calculate the value for k_1 this equation could be rearranged to obtain:

$$k_1 = \frac{C_S(t)}{C_W\, t} \qquad \text{(Eqn. 3.2)}$$

As these values were obtained from laboratory tank tests with known concentrations of the analyte in water (C_w) and samplers were removed at precise times (t) along with after analysis the concentration in the sampler could be determined for each of the times mentioned ($C_s(t)$) it is possible to calculate k^1 for each compound.

The uptake rates were calculated for a selection of pesticides (Table 3.3) and plotted against a variety of different properties to determine which of these effected uptake rates. Under the assumption of stable water concentrations it was assumed that the sampling rate, after a lag period would be linear prior to becoming curvilinear as equilibrium was approaching.

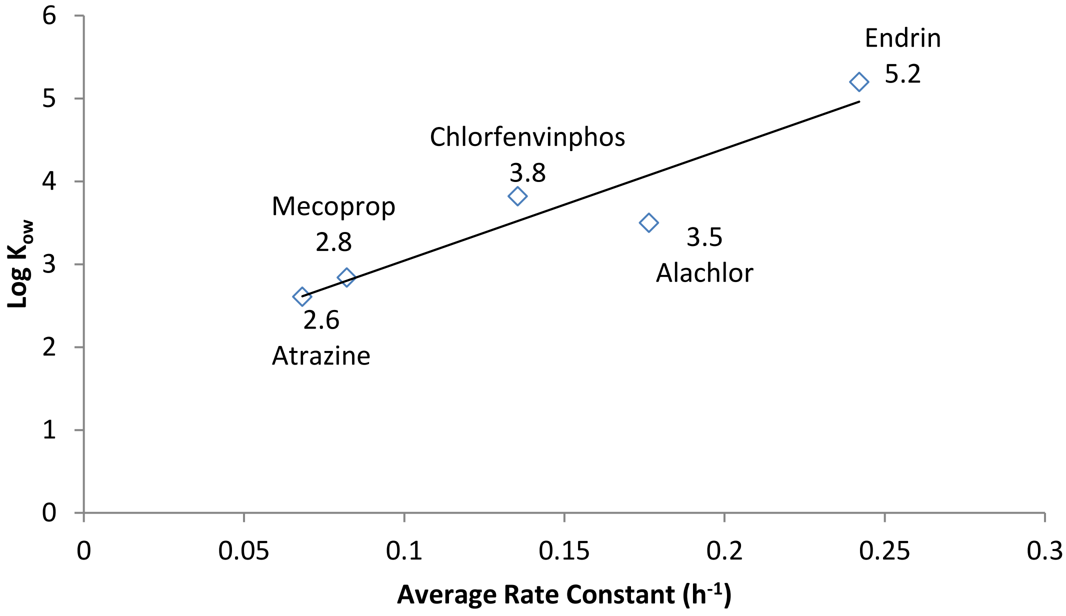
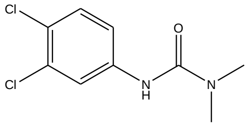
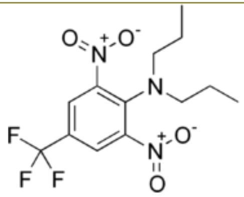


Figure 3.13: Prediction model for kinetic uptake rates of pollutants. Correlation of the average rate constant of five analytes in relation to their Log K_{ow} values. (Equation of the line: y=13.508 + 1.692; r^2: 0.8855) The samples were analysed using a C18 (250 mm x 4.6 mm ID 5 µm Luna column, mobile phase 95:5 v/v acetonitrile:water.

As can be seen a linear correlation is observed when using the pollutants Log K_{ow} value (Range 2.6-5.2) (Figure 3.13). The Log K_{ow} value can be considered to be inversely proportional to the pollutants water solubility. One of the disadvantages that have been mentioned previously to passive sampling is that the concentration of pollutants measured is one the dissolved concentration in the aqueous environment and does not take the concentration adsorbed in the sediment into consideration. For this reason one of the main physical properties that was looked at was the Log K_{ow}. Other properties that were investigated for a correlation include the molecular weight, density and polar surface area along with ratios of these values. When these results were graphed it was found that the correlation was found only for the Log K_{ow} values.

Two other pesticides were selected to determine if the model held true(Table 3.4), and to compare the experimental uptake rates with those that could be calculated based on the predicted uptake rates.

Table 3.4: Selected pesticides to determine the accuracy of the prediction model for kinetic uptake rates.

	Structure	Log K_{ow}	Predicted Uptake Rate	Experimental Uptake Rate	% RSD
Diuron		2.67	0.0724	0.0685	± 3.9%
Trifluralin		5.41	0.2752	0.2835	± 2.1%

As can be seen below good correlation was shown for both pesticides selected during the kinetic regimeFigure 3.14. For diuron and trifluralin the uptake rate stayed linear and therefore it is possible to calculate the sampling rate as a function of hydrophobicity. From this it can be seen that the kinetic uptake rate of pollutants can be determined within the range of approx Log K_{ow} 2.5-5.5. It can be seen that this prediction model is only calculated for the linear kinetic regime. Further studies on prediction models were carried out using MatLab in Chapter 4.

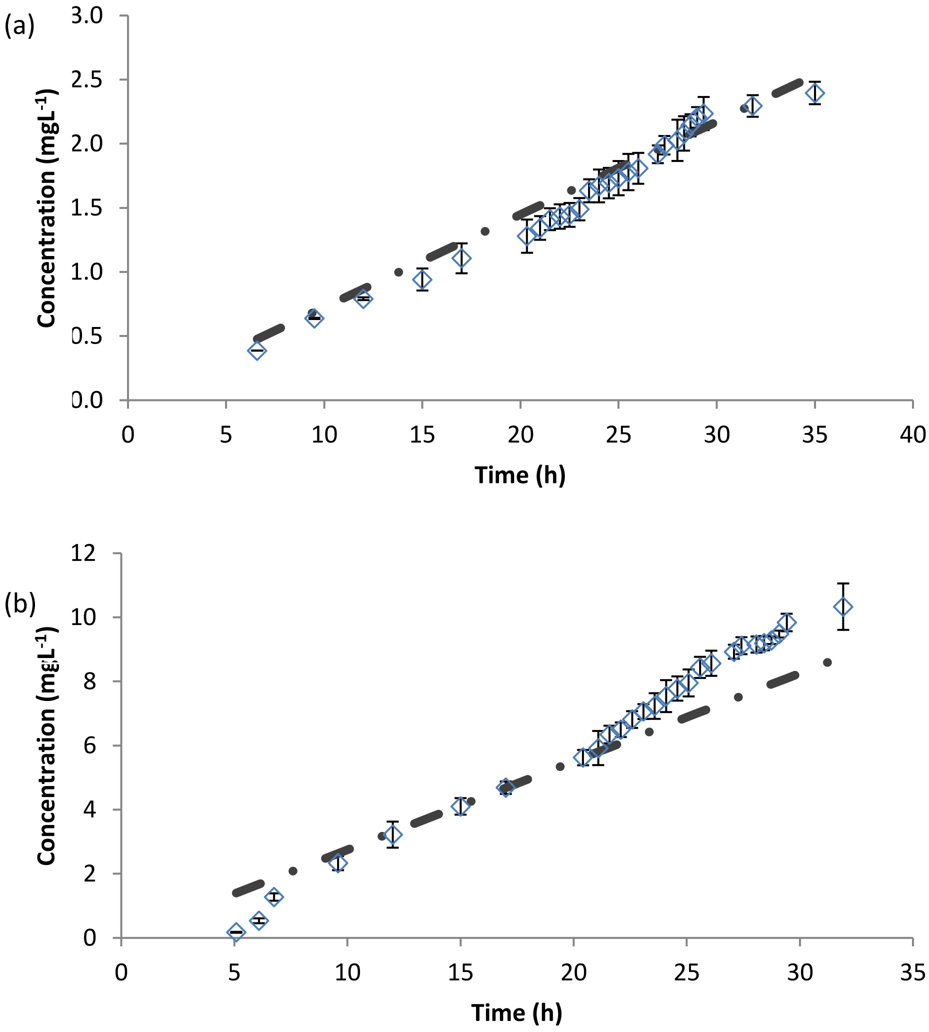


Figure 3.14: Comparison of predicted values (dashed line) and experimental values for the two pesticides selected; diuron (a) and trifluralin (b). (n-3) The samples were analysed using a C18 (250 mm x 4.6 mm ID 5 µm Luna column, mobile phase 95:5 v/v acetonitrile:water.

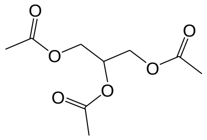
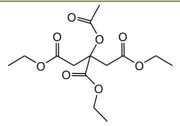
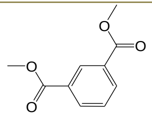
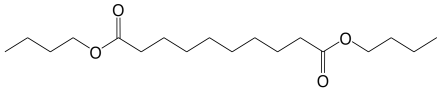
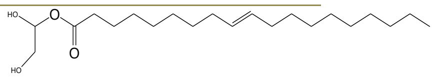
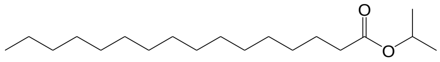
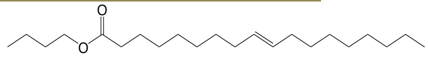
As is shownabove that for the linear uptake regime of the diffusion curve both diuron (Figure 3.14 (a)) and trifluralin (Figure 3.14 (b)) show good correlation with the predicted uptake rate that was calculated previously (Figure 3.13).

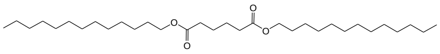
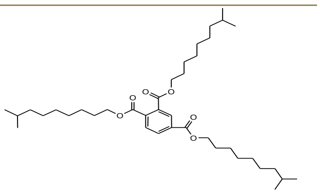
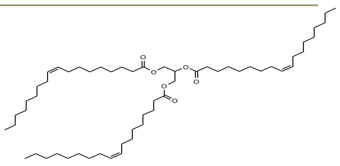
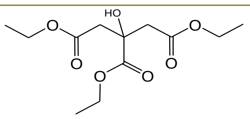
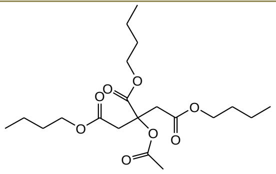
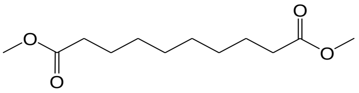
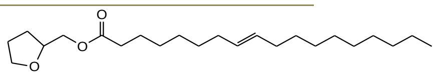
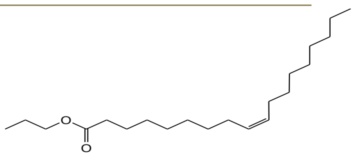
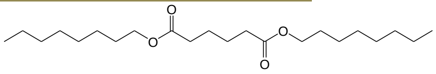
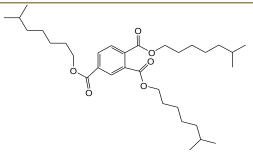
3.3.4 TUNING OF PASSIVE SAMPLING DEVICES

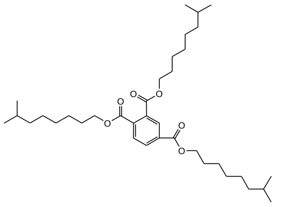
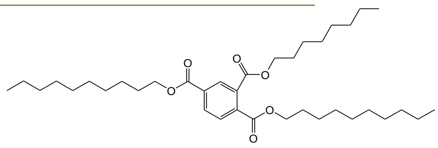
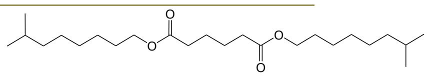
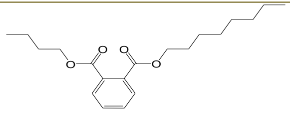
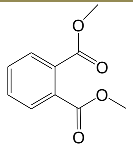
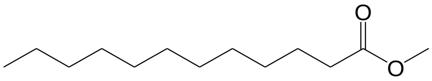
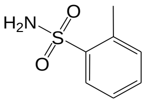
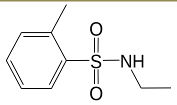
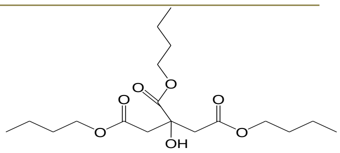
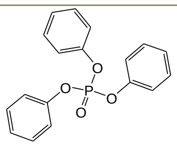
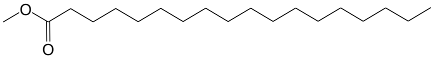
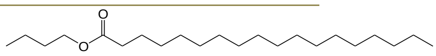
3.3.4.1. SELECTION OF PLASTICISERS

The plasticiser used in the preparation of the novel passive samplers was altered to test 29 distinct variations. This was done for two reasons. Firstly this was carried out to show the effect of the plasticiser to the affinity of the novel passive sampling devices for target analytes. Secondly it was studied to determine if a novel passive sampling device could be developed for selective determination based on chemical and physical properties of the target pollutants. The Log K_{ow} values were obtained by inputting the structure into Chem Office software and calculated the predicted Log K_{ow} (Table 3.5).

Table 3.5: Chemical structures of the selected plasticisers with details of Log Kow, M. Formula and CAS identification number.

	Name	M. Formula	Log K_{ow}	Structure
102-76-1	Glyceryl triacetate	$C_9H_{14}O_6$	0.21	
44-89-4	Acetyl triethyl citrate	$C_{14}H_{22}O_8$	3.73	
1459-93-4	Dimethyl isophthalate	$C_{20}H_{14}O_4$	5.24	
109-43-3	Dibutyl sebacate	$C_{18}H_{34}O_4$	5.98	
25496-72-4	Glycerol monooleate	$C_{21}H_{40}O_4$	6.94	
142-91-6	Isopropyl palmitate	$C_{19}H_{38}O_2$	8.5	
142-77-8	Butyl Oleate	$C_{22}H_{42}O_2$	9.75	

16958-92-2	Ditridecyl Adipate	$C_{32}H_{62}O_4$	13.78	
36631-30-8	Triisodecyl trimellitate	$C_{39}H_{66}O_6$	15.99	
122-32-7	Glycerol trioleate	$C_{57}H_{10}4O_6$	23.71	
77-93-0	Triethyl citrate	$C_{12}H_{20}O_7$	1.49	
77-90-7	Acetyl tri n butyl citrate	$C_{20}H_{34}O_6$	6.92	
106-79-6	Dimethyl Sebacate	$C_{12}H_{22}O_4$	2.79	
5420-17-7	Tetrahydrofurfuryl oleate	$C_{23}H_{42}O_3$	8.14	
111-59-1	n Propyl oleate	$C_{21}H_{40}O_2$	9.22	
108-63-4	Dicapryl Adipate	$C_{22}H_{42}O_4$	8.47	
27251-75-8	Tricapryl trimellitate	$C_{33}H_{54}O_6$	12.48	

53894-23-8	Triisononyl trimellitate	$C_{36}H_{60}O_6$	14.39	
67989-23-5	Tri (n octyl, n decyl) trimellitate	$C_{37}H_{62}O_6$	15.47	
33703-08-1	Diisononyl adipate	$C_{24}H_{46}O_4$	9.24	
84-78-6	Butyl octyl phthalate	$C_{20}H_{30}O_4$	6.95	
131-11-3	Di methyl phthalate	$C_{10}H_{10}O_4$	1.64	
111-82-0	Methyl Laurate	$C_{13}H_{26}O_2$	5.49	
1333-07-9	o,p-Toluenesulfonamide	$C_7H_9NO_2S$	0.79	
1077-56-1	n-Ethyl-o,p-toluenesulfonamide	$C_9H_{13}NO_2S$	1.96	
77-94-1	Tri n butyl citrate	$C_{18}H_{32}O_7$	4.68	
115-86-6	Triphenyl phosphate	$C_{18}H_{15}O_4P$	4.1	
112-61-8	Methyl stearate	$C_{19}H_{38}O_2$	8.68	
123-95-5	n Butyl stearate	$C_{22}H_{44}O_2$	10.27	

3.3.4.2 TESTING OF PLASTICISED POLYMERIC DISKS WITH PRIORITY POLLUTANTS

Three tanks were each spiked with a concentration of 1 mgL^{-1} of an individual priority pollutant, atrazine, dieldrin and flouranthene. A series of plasticised polymeric disks (Table 3.1) were prepared and exposed in these tanks for a period of 24 h prior to removal and extraction as detailed previously (Section 3.3.2.2). The extracts were analysed using the analytical method previously outlined (Section 2.5.2) .

Table 3.6: Results from exposure study of plasticised polymeric disks to three priority pollutants. The samples were analysed using a C18 (250 mm x 4.6 mm ID 5 µm Luna column, mobile phase 95:5 v/v acetonitrile:water.

CAS Number	Name	Log K_{ow}	Atrazine Conc. (mg L^{-1})	Fluoranthene Conc. (mg L^{-1})	Dieldrin Conc. (mgL^{-1})
102-76-1	Glyceryl triacetate	0.25	10.57	4.78	45.51
44-89-4	Acetyl triethyl citrate	3.73	14.73	1.55	-
1459-93-4	Dimethyl isophthalate	5.24	8.60	0.18	-
109-43-3	Dibutyl sebacate	5.98	8.67	0.59	21.81
25496-72-4	Glycerol monooleate	6.94	5.56	2.12	57.07
142-91-6	Isopropyl palmitate	8.5	11.84	2.63	189.12
142-77-8	Butyl Oleate	9.75	10.23	4.99	150.67
16958-92-2	Ditridecyl Adipate	13.78	3.33	1.32	78.70
36631-30-8	Triisodecyl trimellitate	15.99	4.97	> LOQ	12.55
122-32-7	Glycerol trioleate	23.71	1.22	0.56	-
77-93-0	Triethyl citrate	1.49	6.87	0.17	-
77-90-7	Acetyl tri n butyl citrate	6.92	12.43	1.29	1.64
106-79-6	Dimethyl Sebacate	2.79	8.14	0.05	8.75
5420-17-7	Tetrahydrofurfuryl oleate	8.14	5.95	8.88	88.11
111-59-1	n Propyl oleate	9.22	14.94	-	70.90
108-63-4	Dicapryl Adipate	8.47	13.78	7.34	52.39
27251-75-8	Tricapryl trimellitate	12.48	37.24	> LOQ	-

53894-23-8	Triisononyl trimellitate	14.39	6.85	-	40.65
67989-23-5	Tri (n octyl, n decyl) trimellitate	15.47	10.00	3.41	14.18
33703-08-1	Diisononyl adipate	9.16	18.51	4.03	33.46
84-78-6	Butyl octyl phthalate	6.95	8.11	0.49	6.08
131-11-3	Di methyl phthalate	1.64	7.44	0.43	1.45
111-82-0	Methyl Laurate	5.49	7.34	0.32	1.03
1333-07-9	o,p-Toluenesulfonamide	0.79	1.78	-	-
1077-56-1	n-Ethyl-o,p-toluenesulfonamide	1.96	1.56	-	-
77-94-1	Tri n butyl citrate	4.68	5.73	0.52	0.98
115-86-6	Triphenyl phosphate	4.1	16.58	0.24	-
112-61-8	Methyl stearate	8.68	2.77	0.82	0.62
123-95-5	n Butyl stearate	10.27	4.70	-	41.16
	Unplasticised PVC		2.72	0.27	22.11

As can be seen above atrazine was the only pollutant out of three tested to show enrichment into all 30 configurations of the polymeric disks (Table 3.6). From looking at the concentration of atrazine in the extract a pre concentration factor can be noted, in all cases a factor of at least 1 was noted. The lowest preconcentration factor that was found for atrazine was 1.22 (glycerol trioleate) with the highest being 37.23 (tricapryl trimellitate). The second best performing plasticiser for atrazine was found to be diisononyl adipate which has been used extensively (Chapter 3, Chapter 5, Chapter 6) within the scope of this project.

When looking at the results obtained for tricapryl trimellitate it can be seen that use of this plasticiser displays a huge degree of selectivity. From the results obtained for the other two pollutants with this plasticiser it was found at levels below LOQ for fluoranthene and was not detected on the extracts post exposure to dieldrin. When looking at the water solubility of these three analytes it can be seen that atrazine is the most water soluble and dieldrin the least. This shows that if a novel plasticised passive sampler was required for very water soluble compounds a Log K_{ow} selective plasticiser could be prepared.

Fluoranthene was detected in 25 of the 30 novel passive samplers detected. Out of the three compounds tested it displayed the lowest pre-concentration factors. The lowest quantifiable concentration was observed in the extract doped with dimethyl sebacate (0.5 mgL^{-1}). The largest pre-concentration factor that was determined was found for tetrahydrofuffuryl oleate (8.88). Diisononyl adipate which had previously been concentrated on (Section 3.3.1 and Section 3.3.2) showed a pre-concentration of 4.03. One issue that was noted with all of the novel passive samplers in relation to fluoranthene was that selectivity to the same degree as that found for atrazine or dieldrin was not observed (Table 3.6).

The results obtained for dieldrin showed the largest pre-concentration factors out of the three pollutants tested. This has previously been noted in relation to atrazine (Section 3.3.4). The lowest pre concentration found for dieldrin was 0.62 (Methyl Stearate) where the largest calculated pre concentration factor was 189.12 (isopropyl palmitate).

Dieldrin was only detected in 22 out of 30 novel passive samplers tested (Table 3.6). This shows that with an increase in Log K_{ow}, and therefore a decrease in water solubility, several of these passive samplers will not show affinity for the pollutants. It is interesting to note that while there are several plasticisers that did not show enrichment of both compounds in common, there were others that showed preference of one over the other. This shows that the enrichment occurring is not singly down to the water solubility of the compound but also to interactions between the pollutant and the available plasticiser molecules. The two novel passive samplers that did not show enrichment of both dieldrin and fluoranthene were the two sulphonamide based plasticised samplers.

It had been hoped that inclusion of the sulphonamide based plasticisers would show good enrichment of the three compounds as the sulphonamide functional group in the basis of several antibacterial drugs (31). Taking into account the properties reported for this family of compounds it was believed that they could have shown good anti fouling properties which would be a benefit for long term deployment of the novel passive samplers.

Out of the 30 plasticised passive samplers developed (Table 3.6) three were selected for further study. The three selected are the plasticisers that showed the greatest pre concentration of the target pollutants; isopropyl palmite, tetrahydrofurfuryl oleate and tricapryl trimellitate.

3.3.4.3 EFFECT OF SURFACE AREA ON ENRICHMENT OF POLLUTANTS

A study was undertaken to investigate the effect of surface area on the pre concentration factor of the analytes. This was important as increasing the pre concentration factor will in turn increase the sensitivity of the novel passive sampling device during environmental deployment.

In the case of each of the three plasticised passive sampling devices selected above (Section 3.3.4.2) a large uniform sheet of polymeric material was cast. This was done utilising the methods outlined previously (Section 3.3.2.1) but producing a sampler on a much larger scale. This material was then resized into a series of different samplers each with different surface areas.

These samplers were deployed in the same way as previous samplers (attached to string to then deployed). The samplers were exposed for a period of 24 h prior to extraction with 1 mL of IPA and HPLC analysis (Section 2.3.3.2).

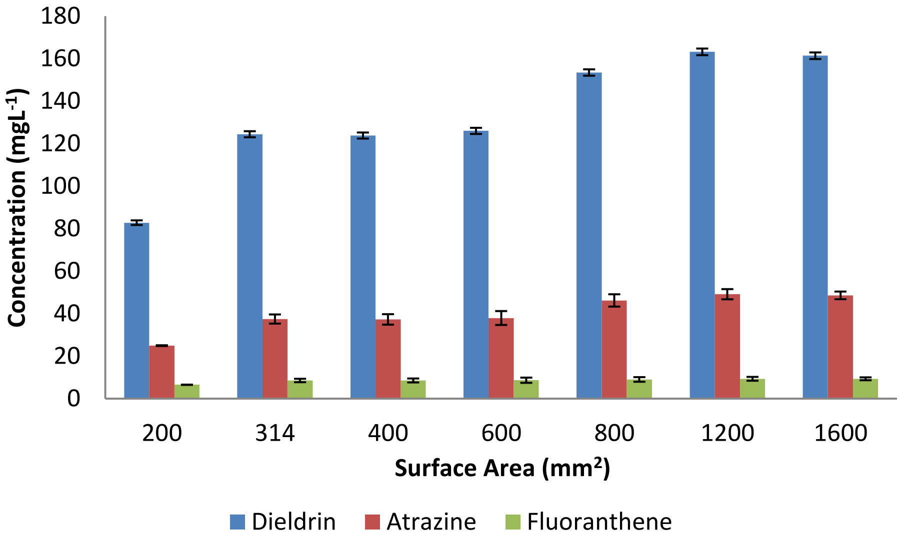


Figure 3.15: Results obtained post exposure of three distinct configurations of novel passive samplers after exposure to the three target pollutants for a period of 24 h. The samples were analysed using a C18 (250 mm x 4.6 mm ID 5 µm Luna column, mobile phase 95:5 v/v acetonitrile:water.

It can be seen from the results above that with increase in surface area an increase in pre concentration of pollutant was observed(Figure 3.15). This was seen to remain at a consistent concentration when the surface area was varied between 314 and 600 mm^2, and a similar trend was noted from 800-1600 mm^2. One issue that arose with the samplers as they increased in size was during the extraction process. These materials were too large to fit into the extraction vials and remain covered when extracted with 1 mL of IPA. For this reason the materials were cut into smaller segments to allow for complete coverage of the polymeric membrane.

One reason that the material appears to level out over a period of 300 mm^2 and 800 mm^2 is not solely down to increased surface area. By increasing the surface area more polymeric material was used and in doing so the bulk of the sampler increased. There have been reports of increased surface area leading to increased sampling rates (32). With both the increase in surface area and bulk of material there is an increase in available plasticiser molecules. These molecules will then form intermolecular forces with the pollutants which will allow for the detection of pollutants within environmental samples.

Out of the surface areas tested the best results were obtained when they increased over 800 mm^2. A recommendation would be that if the novel passive samplers were required for long term environmental exposure, or to exposure where high levels of the pollutant was expected, that an increase in the surface area of the sampler would aid in this enrichment scenario.

3.3.4.3 ENRICHMENT OF POLLUTANTS INTO NOVEL PASSIVE SAMPLING DEVICES

3.3.4.3.1 ATRAZINE

1 mgL^{-1} of atrazine was prepared in a lab based tank. A series of tricapryl trimellitate passive sampling disks were prepared and exposed over a period of 70 h. These samplers were then removed at distinct time points, extracted with IPA for 50 min (Section 3.3.2.2) prior to analysis using HPLC (Section 2.3.3.2.1)

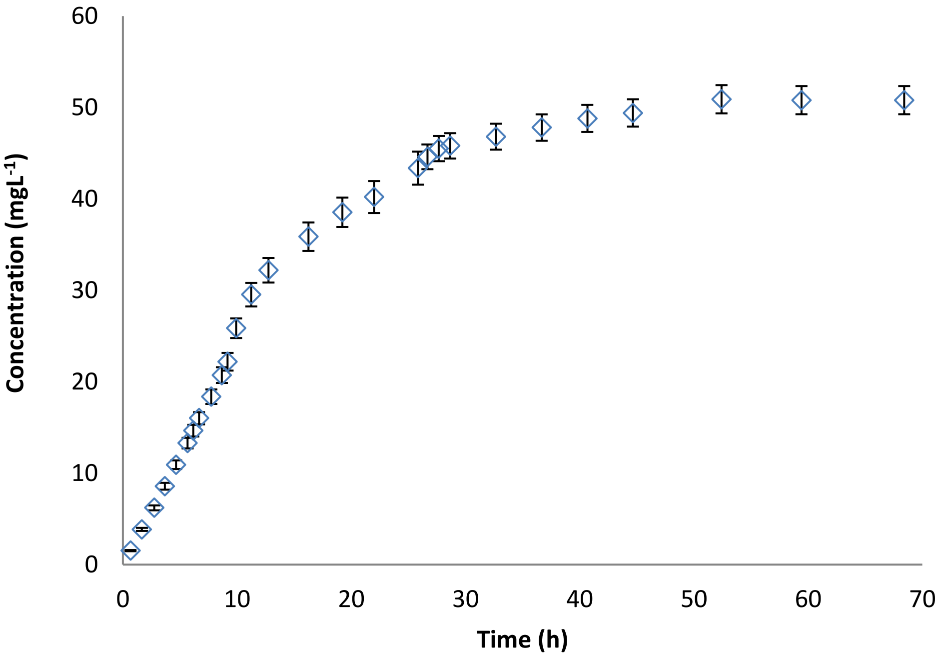


Figure 3.16 Diffusion curve of 1 mgL^{-1} of atrazine into a novel passive sampler doped with tricapryl trimellitate. The samples were analysed using a C18 (250 mm x 4.6 mm ID 5 µm Luna column, mobile phase 95:5 v/v acetonitrile:water.

Out of the three compounds studied for their diffusion into the novel passive sampling devices selected previously (Section 4.3.2)atrazine showed the slowest diffusion. The calculated equilibrium concentration obtained was 52 mgL^{-1} after a period of 52.4 h. T$_{90}$ was reached after a period of 32.6 h.

3.3.4.3.2 DIELDRIN

1 mgL^{-1} of dieldrin was prepared in a lab based tank. A series of isopropyl palmitate passive sampling disks were prepared and exposed over a period of 35 h. These samplers were then removed at distinct time points, extracted with IPA for 50 min (Section 3.3.2.2) prior to analysis using HPLC (Section 2.3.3.2.1)

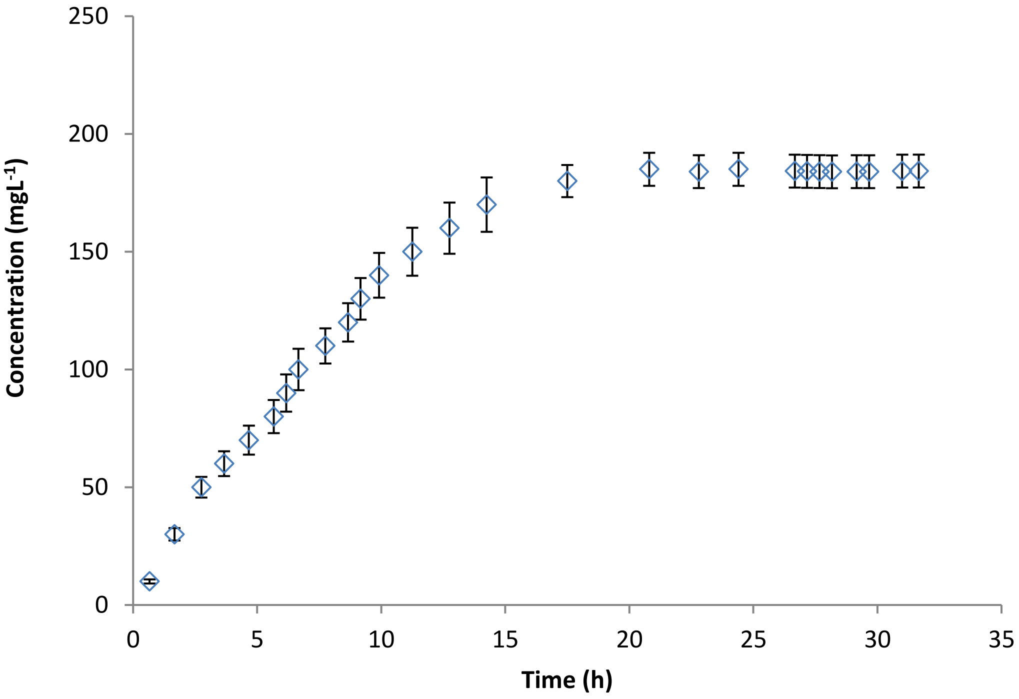


Figure 3.17: Diffusion curve of 1 mgL^{-1} of dieldrin into a novel passive sampler doped with isopropyl palmitate. The samples were analysed using a C18 (250 mm x 4.6 mm ID 5 µm Luna column, mobile phase 95:5 v/v acetonitrile:water.

When looking at the diffusion curve obtained for dieldrin the calculated equilibrium concentration obtained was 184.3 mgL^{-1} after a period of 20.8 h. T$_{90}$ was reached after a period of 12.75 h. This concentration shows a degree of pre concentration greater to that seen with atrazine or fluoranthene (Figure 3.15 & Figure 3.16). This correlates to results seen previously for the diffusion of dieldrin into the isopropyl palmitate (Table 3.6).

3.3.4.3.3 FLUORANTHENE

1 mgL^{-1} of fluoranthene was prepared in a lab based tank. A series of tetrahydrofurfuryl oleate passive sampling disks were prepared and exposed over a period of 35 h. These samplers were then removed at distinct time points, extracted with IPA for 50 min (Section 3.3.2.2) prior to analysis using HPLC (Section 2.3.3.2.1)

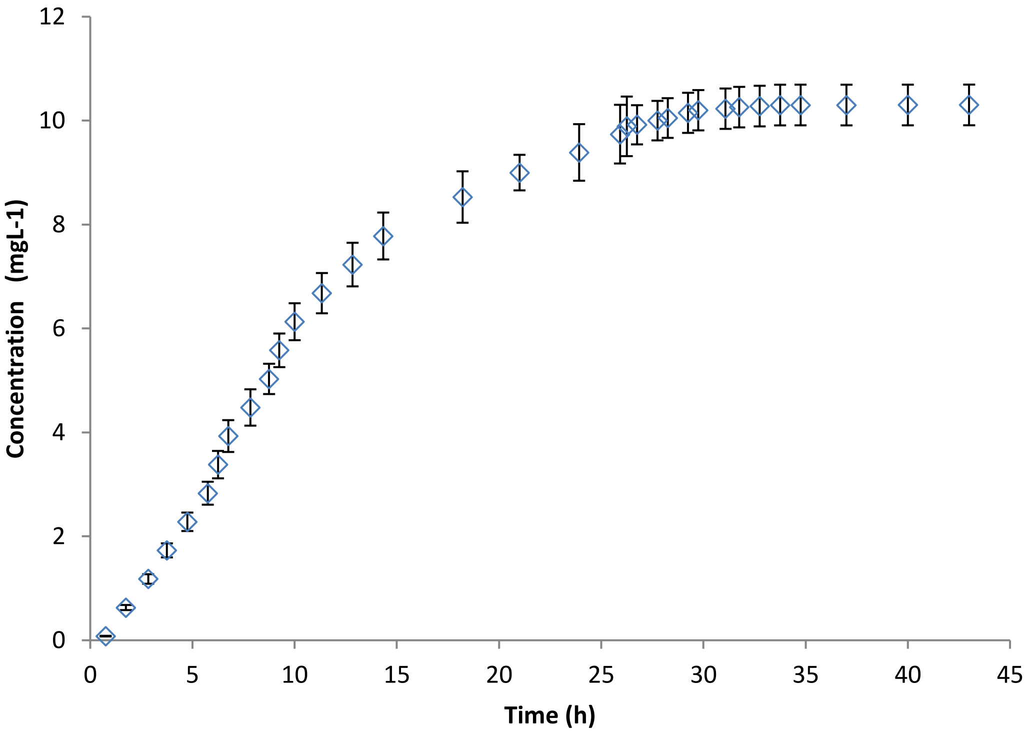


Figure 3.18: Diffusion curve of 1 mgL^{-1} of fluoranthene into a novel passive sampler doped with tetrahydrofurfuryl oleate. The samples were analysed using a C18 (250 mm x 4.6 mm ID 5 µm Luna column, mobile phase 95:5 v/v acetonitrile:water.

Out of the three analytes studied here, fluoranthene showed the lowest pre concentration factor (Table 3.6). The calculated equilibrium concentration obtained was 10.3 mgL^{-1} after a period of 33.75 h. T_{90} was reached after a period of 23.9 h.

From looking at the enrichment of the three pollutants it can be seen that the diffusion in to the three distinct passive samplers follow a Fickian curve as has been reported previously (Chapter 1). When looking at the length of time that the pollutants diffused into the membrane before reaching equilibrium it can be seen that atrazine took the longest time period (55 h) whereas dieldrin took the shortest (20.8 h). This shows that the sampling rate of dieldrin was the largest. As an increase in Log K_{ow} was noted for the analytes and increase in sampling rate was observed.

3.4 CONCLUSIONS

A polymeric material was developed and tested for the enrichment of pesticides and has seen favourable results. Initially a glass mounted polymer membrane was used as the passive sampler. It was hoped that this would find analytical use both on the ATR for a rapid determination of pesticides characterised by their fingerprint regions, and also for a more in depth analysis using GC-MS. Problems were encountered initially with the ATR as the film, despite using the provided weight, would not remain compressed onto the ZnSe crystal. There were two remaining issues with this prototype namely the pre-concentration factor noted was not significantly high enough to confer the degree of sensitivity required, and secondly as the films were cast on glass microscope slides it was difficult to expose them to environmental conditions, with the films peeling of the slides, which affected the uptake rates of analytes.

After the glass mounted polymer membranes were deemed inappropriate a second prototype was developed. This prototype, the novel passive sampling disks, was optimised slightly by varying the percentage of the plasticiser (w/w). The most effective and reproducible method was found to be the casting of the disks in a glass cylinder and leaving the polymeric solution to cure over night prior to removal of disk. These novel samplers were then used to study the enrichment of a variety of pesticides, and in turn a model was developed that enabled kinetic sampling rates to be predicted. The empirical equation can be used to calculated sampling rates of compounds with Log K_{ow} values in the range of 2.5 to 5.5, This is invaluable as it can be used for pollutants for which calibration data has not been carried out.

A series of 30 novel passive samplers were studied to observe the enrichment of three pollutants that are mentioned in Annex X of the WFD. Of the three compounds tested atrazine showed enrichment into all of the 30 samplers tested. In the cases of dieldrin and fluoranthene it was noted that there were samplers that did not show enrichment of the analytes. One of the aims of this study was to determine if a novel passive sampler could be developed to selectively enrich target pollutants. In the case of atrazine this was noted. When the novel passive sampler was doped with tricapryl trimellitate atrazine was the only one of the three compounds detected. This may be useful in the determination of more polar compounds e.g. pharmaceuticals and polar pesticides, within the environment. When looking at the results for the other two compounds the same degree of selectivity was not observed.

One issue that has been noted with these novel passive sampling devices is their sensitivity to pollutant concentrations . Through increase of surface area an increase in pre concentration factors was noted for all three distinct passive sampler configurations. Diffusion of the three target pollutants was studied into the three different novel passive samplers developed. These diffusion curves follow the same trend seen in previous work. The diffusion of all three of these molecules followed Fickian predicted behaviour.

Through the use of an external primary plasticiser 29 different configurations of the novel passive sampling disks were tested for the enrichment of three pollutants. It was found that one of these configurations displayed selectivity for compounds with lower Log K_{ow}.

These samplers show great promise for environmental usage, and fall under many of the points required for a good passive sampler, as outlined previously (Chapter 1). They are robust for exposure to the elements, easy to both use and cast, and are cost effective samplers with approximately 100 samplers cast for under €10.

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CHAPTER 4: ATR-FTIR STUDY OF PASSIVE SAMPLER ENRICHMENT

4.1 INTRODUCTION

Analytical infrared (IR) studies are based on the absorption of the electromagnetic radiation by the analyte which lies between 1 and 1000 µm. This range can be divided into three sub sections; near infrared (800 nm-2.5 µm, 12500-4000 cm^{-1}), mid infrared (2.5-25 µm, 4000-400 cm^{-1}) and the far infrared (beyond 25 µm 100-10 cm^{-1}) (1). Near infra red is known to be poor in specific absorptions but is considered as an important method by quality control laboratories. Mid Infrared provides information about the structures of compounds and as such has found use for the identification of organic compounds. Far infrared requires the use of specialized optical materials and sources; using instruments such as Fourier transform spectrometers.

IR results are usually presented as spectra where a ratio of transmitted intensities, with and without the sample, is calculated for each wavelength. The ratio can be given in transmittance or absorbance, which is the logarithm to the base 10 of the reciprocal of the transmittance($A=\log(1/T)$). The values of wavelengths (µm) can also be substituted by equivalent wavenumbers (cm^{-1}). Whilst the IR spectrum is characteristic of the entire analyte molecule there are certain groups of atoms, or functional groups that give rise to bands that appear at or near the same frequency irregardless of the structure of the molecule (2). It is from these bands that structural information on a compound can be obtained. The intensity of the bands, in both pure analytes and in mixtures, are proportional to the concentration of the analytes. This relationship can be measured and expressed through use of Beer Lamberts Law. Through the use of this it is possible to quantify components based on band heights in both single and multi component analysis (1).

IR spectrometers can be divided into two categories; Fourier transform infrared (FTIR) spectrometers and Dispersive type spectrometers (3). For many years an IR spectrum was obtained by passing an IR beam through the sample and scanning the spectrum with a dispersion device (4). The spectrum was scanned by rotating the diffraction grating; the absorption areas were detected and plotted as frequencies versus intensities.

Within the past twenty years FTIR has been extensively developed and provides a number of advantages over the previous dispersive systems (5). Radiation containing all IR wavelengths (5000-400 cm^{-1}) is split into two beams, one beam of fixed length, one of variable length (movable mirror). The varying distances between these two path-lengths result in a sequence of constructive and destructive interferences and due to these variations in intensities – an interferogram. FTIR converts this interferogram from the time domain into one spectral point on the more familiar form of the frequency domain.

There are a number of advantages to FTIR (3). FTIR instruments can have very high resolution (≤ 0.001 cm^{-1}) and since a monochromator is not used in this method the entire radiation range is passed through the sample simultaneously and from this much time is saved. Another main advantage of these systems is that since the data can undergo analog to digital conversion the results can be easily manipulated. By this it is meant that the results of several scans can be combined to average out random absorption events which can result in excellent spectrum from minute amounts of sample (4).

4.1.2 ATTENUATED TOTAL REFLECTANCE (ATR)

ATR is a technique that can be used with IR spectroscopy, and means samples can be examined directly in solid, liquid or gas states (3). ATR accessories are very useful tools to obtain spectra of samples that cannot be easily examined by more common transmission methods. These accessories can be suitable for the study of thick or highly absorbing solid and liquid samples. To run an ATR sample it is important that the sample is brought in good optical contact with the ATR crystal (6) and that it undergoes single or multiple internal reflections. The number of reflections and the penetration depth decrease with increasing angle of incidence.

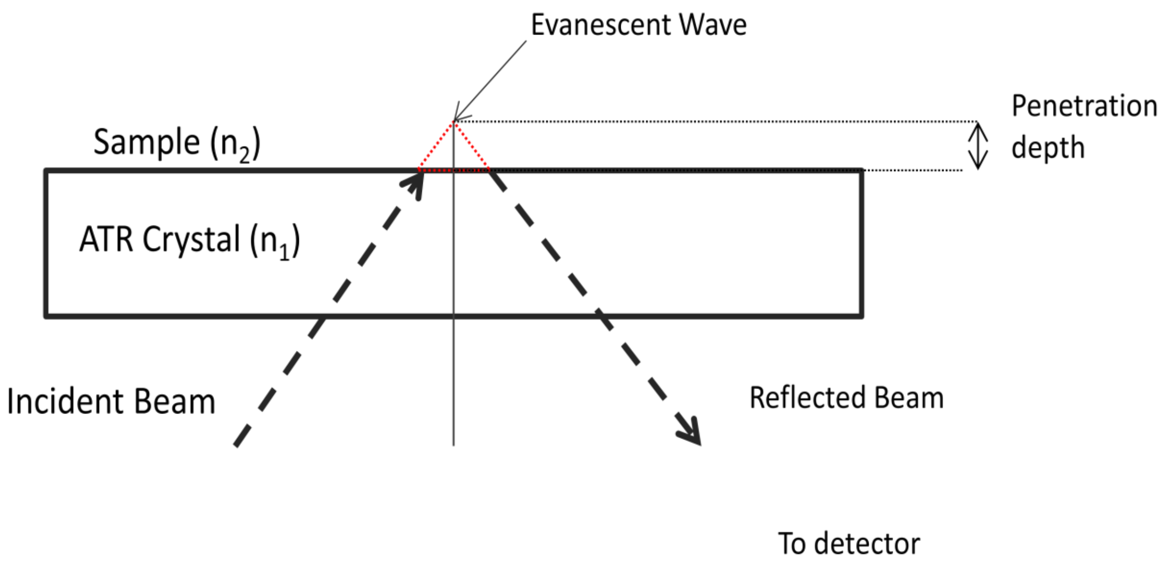

Figure 4.1: Schematic illustration of the principle of the ATR spectroscopic technique: n_1 and n_2 are refractive indices of the ATR crystal and sample material, respectively. Note that condition n1 > n2 is required for the total internal reflection to occur at the ATR-crystal-sample interface. Evanescent wave is represented by the red dotted line. (Adapted from Chemical Analysis 2nd Edition (3))

The principle of ATR is total internal reflection which results in an evanescent wave. ATR occurs when a beam of radiation enters from a denser (higher refractive index) into a less dense (lower refractive index) medium. As the angle of incidence increases so too does the fraction of the incident beam,when the angle of incidence is greater than the critical angle all incident radiation is completely reflected at the interface. The beam then penetrates a short distance beyond the interface and into the less dense medium before complete reflection occurs. This distance is referred to as the evanescent wave and is typically a few micrometers.

There are several factors that will affect the depth of penetration, the wavelength, the refractive index of the sample and the angle of incidence of the beam at the surface. The penetration depth d_p can be calculated using the following formula (7):

$$d_p = \frac{\lambda_0}{2\pi n_2 \sqrt{sin^2\theta - (\frac{n_1}{n_2})^2}} \qquad \text{(Eqn. 4.1)}$$

Where θ is the angle of incidence, λ is the wavelength of radiation (µm), and n_1 and n_2 are the refractive indices of the surrounding medium and of the crystal respectively.

An ATR spectrum is similar to the conventional absorption spectrum with the exception of band intensities at longer wavelengths. At these wavelengths the evanescent field will penetrate even deeper into the sample, equivalent to an increasing sample thickness. It is possible to apply an empirical so-called ATR correction to compensate across the spectrum for the linear wavelength increase which can be seen below.

$$R_{corr} \sim R\frac{1}{\lambda} \qquad \text{(Eqn. 4.2)}$$

Other differences may occur due to surface effects between the sample and the optical crystal or due to absorption changes across the sample. Single reflection of multi-reflection crystals may be used. The measured reflectivity depends on the number of reflections as well as on the efficiency of contact between sample and substrate surface.

The internal reflection element (IRE) is most commonly made from material that has a high refractive index e.g. silver chloride (AgCl), germanium selenide (GeSe), and zinc selenide (ZnSe). These materials are available in a variety of surface areas and entrance angles. ATR crystals for the UV, VIS, and NIR ranges are usually made of quartz glass, whereas sapphire is used for special UV and NIR applications as it is one of the hardest of all optical materials which makes the surface more scratch resistant. For mid IR, the region of this chapters interest, zinc selenide (ZnSe), silicon, germanium and diamond are commonly used. ZnSe is the most popular material for ATR crystals with its most important advantage being its low absorbance at wavelengths larger than 10 µm. However, it should be noted that ZnSe crystals have one major disadvantage over GeSe and silicon crystals in that it scratches much more easily and is deemed toxic. It is for this reason great care should be taken with the use and handling of ZnSe crystals.

The main fields of application of ATR are metals, polymers, rubbers, coatings and interfaces of liquids and solids (1).

4.1.3 APPLICATIONS OF ATR-FTIR

ATR spectroscopy is a well established surface spectroscopic technique that has found a range of applications. One issue that arises when using ATR spectroscopy is the sensitivity of the method. Research has shown that the coating of the crystal, or in cases, an infrared optical fibre, with a polymeric material can improve the sensitivity of this method (8). This is due to the affinity that the analyte will have with the polymeric material. The analyte will then concentrate within the evanescent wave region of the crystal.

When coating the crystal with a polymeric material it is important to consider the characteristics of the coating. The material selected should have an affinity for the analyte, not obscure the region of interest for analytes to be detected and be easily coated and removed from the crystal. The analyte should be able to rapidly diffuse through the coating, which in turn will improve the response time for measurement (8).

One commonly used polymer for this method is PVC. PVC provides a good spectral window, and can easily be cast and removed from solid surfaces. Work has been carried out to determine the effect of the addition of plasticiser to the polymeric material with respect to the diffusion of the target analyte. One group of plasticisers that have been shown to work is the chloroparaffin family. Ertan-Lamontagne *et al.* (8) conducted a study to determine if the incorporation of a chloroparaffin plasticiser decreased the time it took the analytes, nitrobenzene and benzonitrile, to reach T_{90}, and if this addition with increase the value of maximum absorbance. It was found that the plasticized polymer improved both the time response and increased the absorbance value at T_{90} of analyte bands, in doing so increasing the sensitivity of the optical technique (8). Various formulations of this chloroparaffin based polymeric material were then tested for response time and sensitivity of target analytes. A comparison between unplasticised PVC, PVC with 23% chloroparaffin (60% Cl), PVC with 33% chloroparaffin (60% Cl), PVC with 41% chloroparaffin (60% Cl) and PVC with 47% chloroparaffin (60% Cl) was carried out. It was found that not only did the unplasticised PVC have the longest response time but it also had the lowest sensitivity where it did not reach maximum absorbance after being in contact with the solution for 80 min. It was also noted that an increase in plasticiser concentration led to a decrease in response time, and an increase in sensitivity with PVC and 47% chloroparaffin (60% Cl), response time by approximately 25 min showing the best performance of the materials tested. One explanation for this phenomenon is that the increase in the rate of equilibrium can be attributed to the increase in fluidity (lowering of T_g) in the polymeric phase. Another factor to note is that the diffusion of the analyte is dependent on the affinity of the analyte upon the polymeric material.

Further work was carried out with PVC/Chloroparaffin coatings for ATR-FTIR by Regan *et al.* (9) for the determination of pesticides in water. The target analytes selected were atrazine, alachlor and p’p’-DDT which are all mentioned in Annex X of the WFD. It was previously thought that the ATR surface should have a thick hydrophobic layer coating in order to eliminate the water absorption bands. It was found however, that by using a very thin layer < 5 µm in thickness, and saturating this material with water prior to analysis that satisfactory absorbencies and response times were determined for the analytes. The polymeric material was tested over a range of chloroparraffin concentrations, 0-10%, for both atrazine and alachlor. From this it was seen that a chloroparaffin concentration of 5% showed the optimum results as after this point the maximum absorbance from analytes started to deteriote. Furthering on from this study the concentration of PVC, 0.3%, 2%, 1% and 6%, was varied to determine the effect on the diffusion of analytes. Whilst initially the increase in percentage PVC correlated with an increase in maximum absorbance, once the percentage increased past 1% this trend was decreased. This can be explained by looking at the evanescent region of the ATR element. As the percentage of PVC increased, so too did the thickness of the polymeric membrane, which in turn led to the longer time needed by the analyte to diffuse into the evanescent region. This can be seen clearly in the results obtained by the 6% PVC membrane, after a period of approx. 70 min the analytes had yet to reach equilibrium. In contrast the T_{90} was reached for the 0.3%, 1% and 2% in approximately 7, 8.5, and 10 min respectively. This work showed that the polymeric material also acted as a pre-concentrating medium for the analytes with enrichment factors of 30 and 20 for alachlor and atrazine respectively. From this detection limits for the analytes were determined to be in the region of 2 mgL^{-1} which shows the use for this type of spectroscopic analysis.

Another polymer that has found use in polymeric material ATR is Teflon®. Murphy *et al.* (10) studied the diffusion of toluene, chlorobenzene and 1,3-dichlorobenzene, into Teflon ® AF2400. A calibration curve was found to be linear in the range of 50-300 mgL^{-1} when measured through four distinct bands that can be attributed to toluene. Some of these bands showed greater sensitivity (1231 cm^{-1}) than others (1302 cm^{-1}). When looking at the absorbance of the three target compounds it was noted that an increase in chlorine atoms on the molecule (0, 1, 2) showed an increase in absorbance for the band intensity. It can be seen that as the increase in absorbance is noted so too is a decrease in water solubility. From this it can deduced that 1,3 dichlorobenzene has the greater affinity for the hydrophobic polymer layer. The difference between the other two compounds is not as marked as for 1,3 dichlorobenzene and this can be seen that the decrease in water solubility between toluene and chlorobenzene is less significant, 515 mgL^{-1} to 500mg L^{-1} than that for 1,3 Dichlorobenzene (69 mg L^{-1}).

More recently Dobbyn *et al.* (11) illustrated the rates of diffusion of halomethanes into polymer membranes using ATR spectroscopy. The polymer membranes were tested for compounds that included chloroform, bromoform, bromodichloromethane, and dibromochloromethane. Each of these compounds had an infra-red band selected from the fingerprint region that was unique to that molecule in such a way that for multi-component systems these bands did not overlap and obscure other bands of interest. Diffusion coefficients were calculated using a Fickian type mathematical model which assumes that there is a constant flow of analyte and therefore a constant concentration of analyte remaining at the polymer interface. This model also took in several other factors that would affect the diffusion of analytes such as the refractive indices of both the ATR and polymeric medium, the thickness of the film and the wavelength of the quantified peak. These factors are important as the diffusion coefficient has been seen to vary with polymer thickness (12), and the penetration depth obtained for the material will vary with the wavelength (13). It was shown that the experimental diffusion curve obtained correlated positively with the predicted model calculated.

4.1.4 AIMS AND OBJECTIVES

The aim of the work in this chapter is to illustrate that the diffusion of select analytes into the passive sampling membrane follows a Fickian diffusion curve, and also to develop a model that enabled the calculation of the diffusion coefficient of the target analytes. An important element of this work is to illustrate the differences in enrichment that occurs when more than one pollutant is present. To illustrate this both single- component and multi-component analysis was carried out.

The work was carried out using polymer coated ATR spectroscopy, which allowed for rapid analysis of samples. Diffusion coefficients for the analytes were calculated using a script written for Matlab by Nina Hanzlikova (Appendix I). The effect of multi-component diffusion is also investigated in regards to absorbance values at equilibrium, diffusion coefficients and T_{90} values for the target analytes.

4.2 MATERIALS AND METHODS

4.2.1 POLYMERIC MATERIAL

The polymeric material was prepared by slowly adding 5% w/v PVC into THF with 50% w/w of diisononyl adipate. The solution was stirred with a magnetic stir bar until completely dissolved (approx 2 h).

4.2.2 STOCK SOLUTIONS

Due to the low solubility of the target analytes in water the stock solutions used for the following studies contained 4% methanol. The selected analytes were initially dissolved in the methanol and then DI H_2O was used to fill to the mark. The volumetric flask was stoppered and inverted several times to homogenise the solution.

4.2.3 CASTING OF POLYMER

A 1000 µL pipette tip was cut to the point in which a glass pasture pipette could be attached it, and remain attached to the auto pipette whilst the vacuum remained. A 5% PVC polymeric solution with the ratio of polymer to plasticiser that was determined in Chapter 3 was prepared (Section 3.3.3.3). A 100 µL quantity of the polymeric material was cast onto the crystal using the glass pipette as described above and agitated until a smooth film was obtained. This film was left for 11 min prior to use.

4.2.4 INSTRUMENT SET UP

A PerkinElmer Spectrum GX FTIR system was used with an ATR accessory. The software used for this instrument was Spectrum v3.01 © Perkin Elmer 1999. Prior to analysis each time the energy level was checked to ensure it remained within the same range of 1500-1520.

The background taken for the enrichment samples was the passive sampling membrane exposed to water with 4% methanol. This passive sampling membrane was left for minimum 11 min prior to use to ensure complete evaporation of THF (Section 4.2.3).

The following parameters were used in the setting up of the Spectrum software prior to analysis.

Table 4. 1: Parameters used for the IR analysis of target analytes

Parameter	
Range	4000-600 cm^{-1}
Number of scans	4
Resolution	4.0 cm^{-1}
Interval	1.0 cm^{-1}
Units	Abs
Type	Ratio
Gain	2

4.2.4 CALCULATION OF DIFFUSION COEFFICIENTS

Diffusion coefficients of priority pollutants were calculated using a script written for MatLab by Nina Hanzlikova which is detailed in Appendix I.

4.3 RESULTS AND DISCUSSION

4.3.1 CASTING OF POLYMER

Initial studies were carried out using a 15% PVC based polymeric material as developed in Chapter 3, however whilst casting this material it was seen that to obtain a smooth thin film the solution was too viscous. A 5% PVC polymeric solution with the same ratio of polymer to plasticiser that was determined in Chapter 3 (50% w/w) was prepared. Using a 5% PVC solution 200 µL of the polymeric material was cast onto the crystal using the glass pipette as described above and agitated until a smooth film was obtained. This material was then used to analyse the diffusion of 100 mgL^{-1} of alachlor. It was found that after one hour that the absorbance value of the 1062 band associated with alachlor was 0.05448, this is in comparison to the value obtained with 100 µL of the 15% PVC polymeric material where the absorbance was found to be 0.034 for the same exposure time.

It was decided to look at lowering the volume of the material to determine if a thinner film could be obtained, and through this leading to less distance for the analyte to travel to reach the evanvescent region of the polymer membrane. 100 µL of the 5% PVC solution was cast onto the crystal and was used to analyse the diffusion of 100 mgL^{-1} alachlor. After a period of 1 h the absorbance value of 1062 cm^{-1} was seen to be 0.1307. Of the three casting methods tested this method led to the highest absorbance reading which in turn aided in the sensitivity of measurements for further studies. However when it lowering the volume of material deposited even further was looked at the resulting films would not cover the entirety of the crystal.

The reproducibility of this dispensing method was tested using DI H_2O and pippetting a selection of volumes with the glass pasteur pipette attached and then comparing this method to that of pipette tip alone, with results being found to be comparable. The glass pipette was used for one use only. Once 100 µL of the polymeric material was cast onto the ZnSe crystal, this was then swirled around to ensure complete coverage of the crystal.

4.3.1.1 REPEATABILITY OF CASTING METHOD

A study was carried out to investigate the ruggedness of the polymer casting procedure onto the crystal and was carried out at described above (Section 4.2.2). A sample of atrazine was measured, the polymer coating removed and the crystal was cleaned. The polymeric material was then cast onto the crystal again and a sample of atrazine from the same stock solution was analysed again for a period of 1 h.

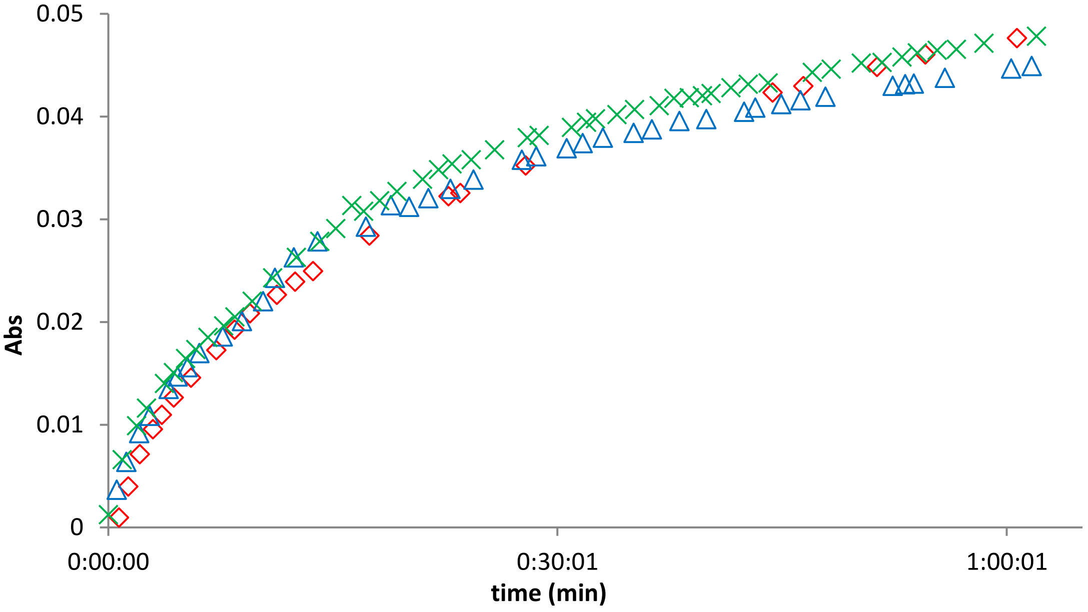

Figure 4.2: Repeatability of the passive sampling membrane using atrazine as a test analyte (run 1:◊; run 2:Δ; run 3:X)(n=3). Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

As the passive sampling membrane is only a one use membrane it is very important to ensure that the coating procedure is repeatable. The mass of the membrane has shown repeatability with the use of a 100 µL volume (5% RSD n=10). The above figure shows the analysis of 100 mgL^{-1} of atrazine using the novel polymeric material (Figure 4.2). As can be seen the absorbance values obtained are reproducible with three distinct coatings of the polymer. The same volume was cast onto the crystal and a film thickness of approximately 44.22 µm ± 5.2% was obtained in each case.

4.3.2 EVAPORATION OF THF

When casting of the polymeric coating on the ZnSe crystal initially, the material was left for approximately four minutes prior to analysis to let the solvent evaporate. From the results obtained on initial work that was carried out using the ATR a reduction in absorbance was found to be quite significant for two peaks 1062 cm^{-1} and 905 cm^{-1} after initial readings. These peaks were later identified to be part of the THF spectrum and assigned to the C-O-C Vibration and the C-C ring stretch present in the molecule respectively. From this it was concluded that the THF had previously not been giving sufficient time to evaporate fully before the spectra of the DI H_2O with 4% methanol background, or the analyte of interest were obtained. This was an issue due to the broadness of the peaks, which served to obstruct several peaks of interest in the target analytes. In this study an air background of the ZnSe crystal was taken and then the polymeric material was cast on to the crystal. Scans were taken regularly over a 15 min period and the decrease in absorbance can be clearly seen below (Figure 4.3)

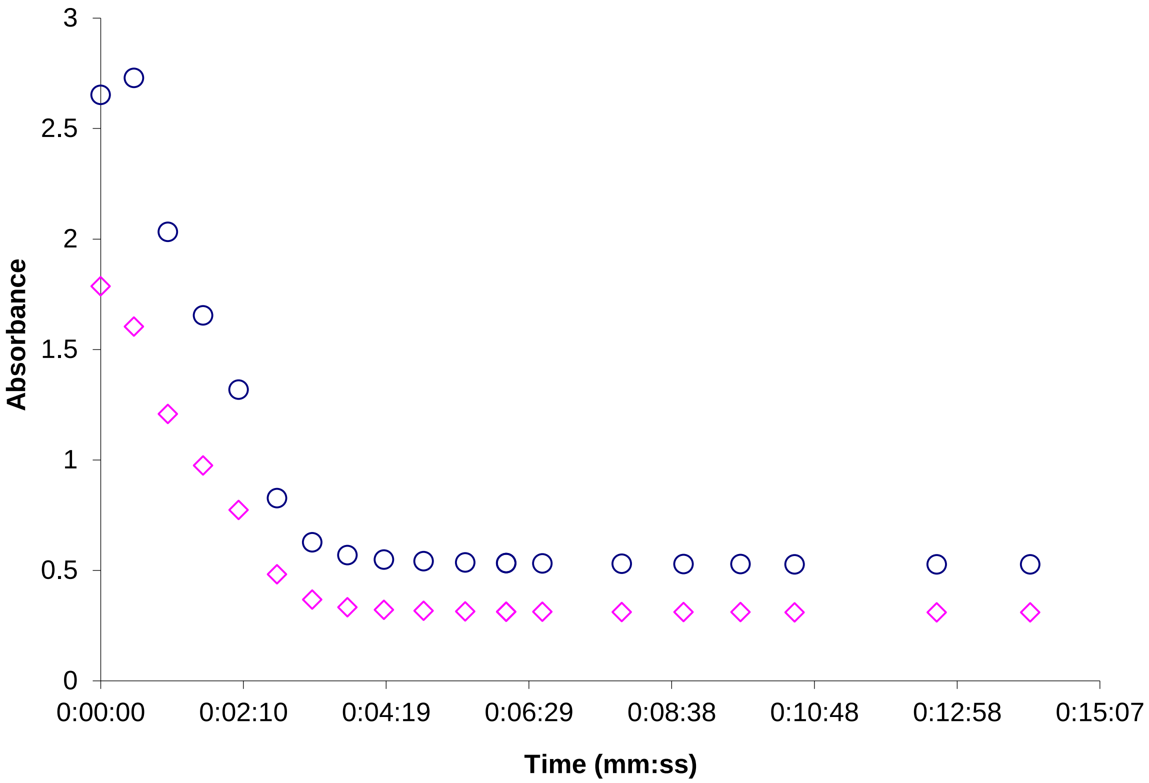

Figure 4.3: Evaporation of THF from passive sampling membrane. This graph shows the evaporation of two peaks that correlate to THF peaks (1062 cm^{-1} (o) and 905 cm^{-1} (◊)) decreasing over a period of 11 min. Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

As can be seen above the evaporation of THF appears to level off at approximately 4.5 min (Figure 4.3). However, on closer inspection it can be seen that though the decrease in absorbance is significantly slowed down it will still have a significant impact in the resulting spectrum.

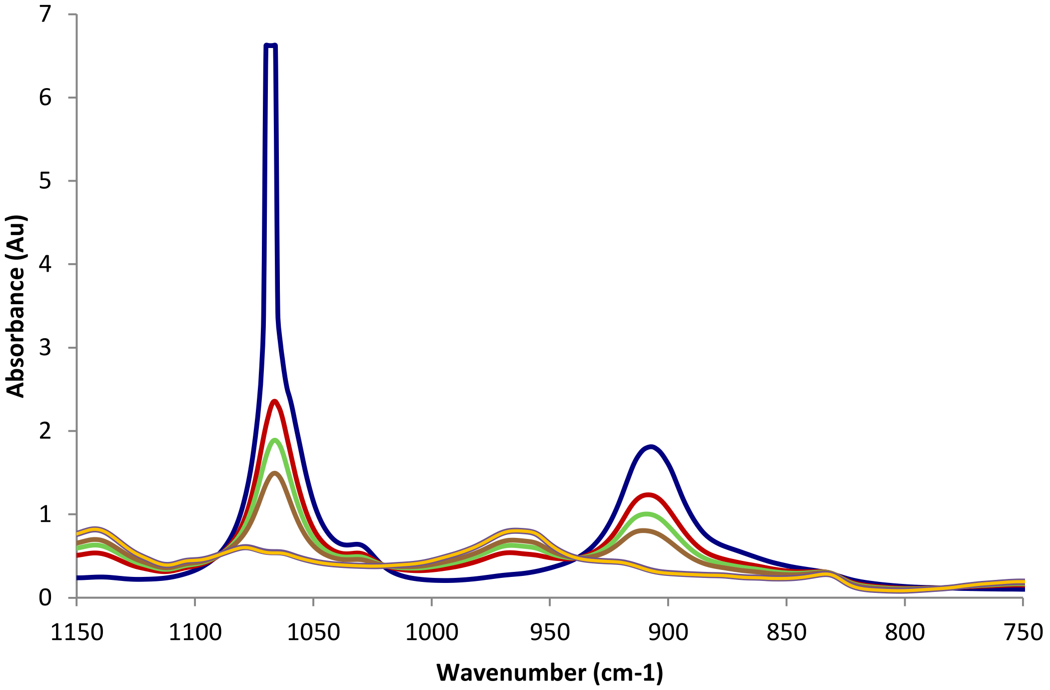

Figure 4.4: Overview of THF bands of interest (1062 cm^{-1} and 905cm^{-1}). It can be noted that a decrease in absorbance is observed for both of these bands over a series of time points (Start time (blue); 1 min (red), 1.5 min (green), 2 min (brown), 5 min (grey), 10.75 min (yellow). Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

The evaporation of THF completely levels of at the 10.75 min mark (Figure 4.4 – yellow band). As mentioned previously the decrease in absorbance appears to level off at 4.5 min however as can be seen above that the absorbance at 10.75 min (yellow) is minutely lower than that at 5 min (grey).

For all further experiments the passive sampling material was cast on and left for a minimum of 11 min before the DI H_2O water with 4% methanol was used to obtain the background scan.

4.3.4 THICKNESS OF FILM

The polymeric material was made using the method mentioned previously (Section 4.2.1). This material was then coated onto one side of the ATR crystal, (trapezoidal design, zinc selenide, 8 internal reflections, 45° entrances angle. The crystal was mounted on a metal block which allowed liquid to be deposited onto the coated crystal. The resulting dimensions of the oblong shape where 1.2 cm width, length 4.4 cm, and surface area 4.971 cm^2. The polymer membrane was coated onto the crystal and left dry for a period of 11 min to ensure complete evaporation of THF.

A previous method obtained for the calculation of the polymer thickness involved the weighing of the crystal before and after coating and from this calculating the mass of dried polymeric material deposited on the crystal. However as the crystal was embedded in the trough plate and could not be detached issues arose when attempting this. For this reason the material was cast, left to dry and then removed from the crystal to obtain an accurate weight of the membrane. The thickness of the film was calculated using the following equation (14).

$$Thickness\ (cm) = \frac{weight\ of\ polymer\ membrane\ (g)}{Density\ of\ polymer\ (gcm^3)x\ surface\ area\ of\ crystal\ (cm^2)} \qquad \text{(Eqn. 4.3)}$$

The thickness of the film was calculated to be 0.0044 cm ± 5.2%. This value is the average of the weights of ten distinct polymer membranes.

4.3.5. ENRICHMENT OF ANALYTES

All results detailed in the following section are in the analysis of single analyte diffusion into the novel polymer membrane. The diffusion curve predicted by the model is shown in comparison to the experimental data that was obtained and the best fit was determined.

Absorbance results are based on the height of the peak using 0.0 AU as the baseline for measurements. The response curve of the data was determined based on a model mentioned previously by Murphy *et al.* (10)

$$\frac{A_t}{A_{eq}} = 1 - \frac{8}{\pi d_p (1 - e^{-\frac{2L}{d_p}})} \sum_{n=0}^{\infty} \frac{e^{g}[fe^{-\frac{2L}{d_p}} + (-1)^n \left(\frac{2}{d_p}\right)]}{(2n+1)(\frac{4}{d_p^2} + f^2)} \qquad \text{(Eqn. 4.4)}$$

Where:

$$f = \frac{(2n+1)\pi}{2L}$$

$$g = \frac{-D(2n+1)^2\pi^2 t}{4L^2}$$

Where L is the thickness of the polymer membrane, A_t is the absorbance of the measured band at time t, A_{eq} is the absorbance at equilibrium and d_p is the depth of penetration of the standing infrared evanescent wave. Because all other parameters are known, D can be calculated by regressing experimental data with the above equation.

This formula (Eq. 4.4) is calculated using the one dimensional diffusion process described in Ficks Second Law:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad \text{(Eqn. 4.5)}$$

With the following initial and boundary conditions for a film of thickness 2l (-l to l) is exposed to an infinite reservoir of analyte the following can be shown:

$C=C_0$ at $0<x<l$ $t=0$

$C=C_1$ at $x=l$, $t\geq 0$

$$\frac{\partial C}{\partial t} = 0 \text{ at } x = 0.\, t \geq 0$$

Where C is the analyte concentration, and D (cm^2sec^{-1}) is a concentration averaged mutual diffusion coefficient. One solution of this equation with these boundary conditions is given by (15)

$$\frac{C-C_0}{C_1-C_o} = 1 - \frac{4}{\pi}\sum_{N=0}^{\infty}\frac{(-1)^n}{2n=1}\ x\ exp\frac{-D(2n+1)^2\pi^2 t}{4l^2}\ x\cos\left(\frac{(2n+1)\pi x}{2L}\right). \qquad \text{(Eqn. 4.6)}$$

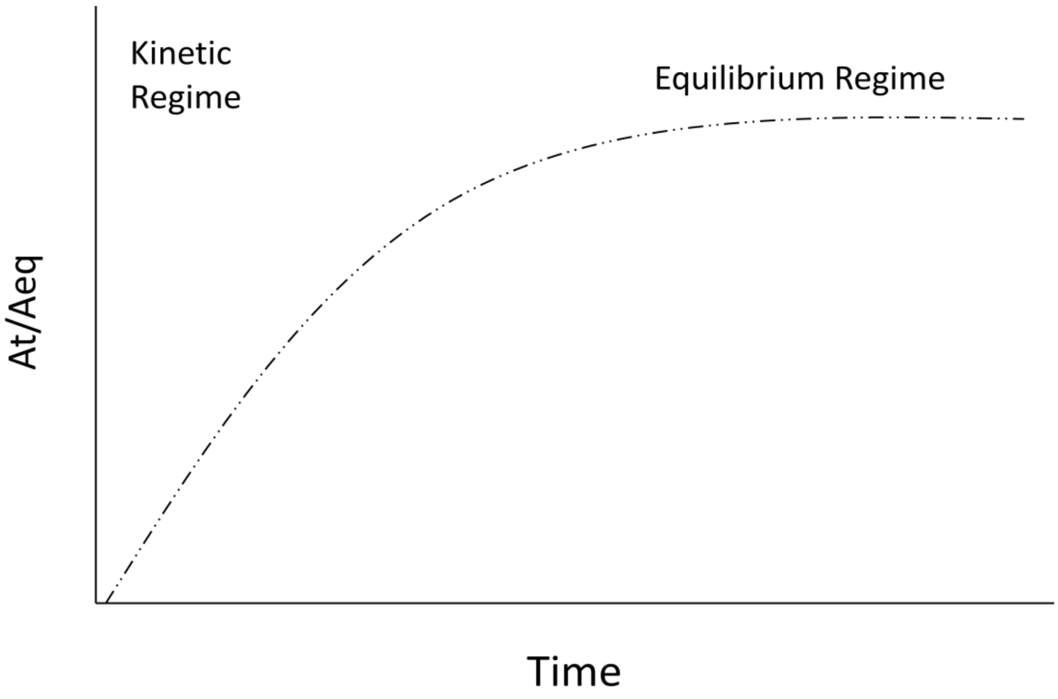

Figure 4.5: Typical Fickian diffusion curve. The ratio of absorbance at time (t) against the absorbance at equilibrium is plotted against time to obtain a Fickian diffusion curve. If the diffusion coefficient of the penetrant is known a predictive curve can be obtained using equation 4.4

A typical Fickian diffusion curve is illustrated above (Figure 4.5). These curves can be split into distinct regions; the kinetic regime and the equilibrium regime as mentioned previously (Section 3.3.1.4). The diffusion curve exhibits a smooth process in which the curve is linear (approximately 60%) before entering into a curvature region prior to reaching equilibrium.

4.3.5.1 ALACHLOR

IR spectra were obtained of alachlor diffusing into the novel plasticized membrane over a period of 7.45 h using the parameters mentioned previously (Table 4. 1). Below a spectrum of the analyte neat is shown (Figure 4.7),and a selection of time points have also been overlaid (Figure 4.7) . What can immediately be noticed when looking at these figures is the increase in absorbance noted for the spectra showing diffusion into the passive sampling membrane (Figure 4.7). This pre concentration of analytes into polymers has been shown previously by Ertan-Lamontagne *et al.* (8) and Regan *et al.* (9) and was observed with all pollutants within this section.

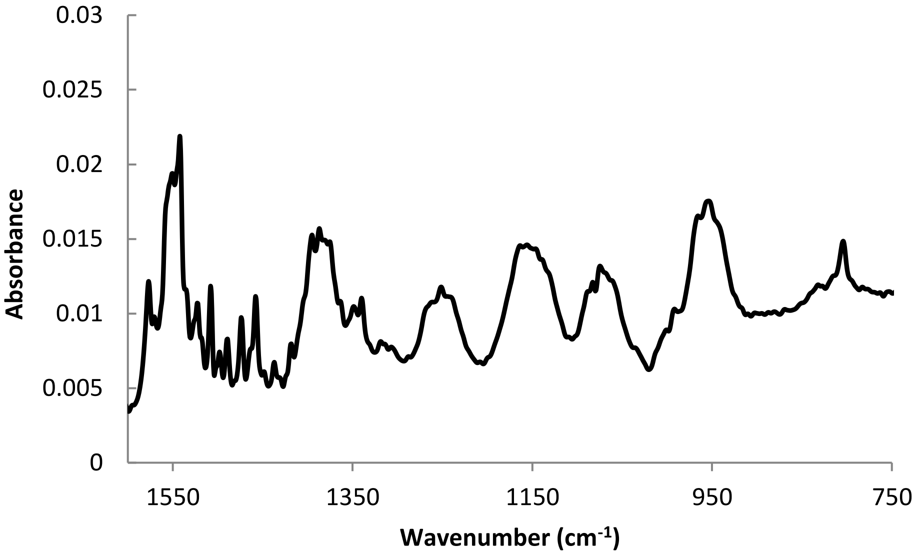

Figure 4.6: Ir spectum obtained for Alachlor. Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

A spectrum of alachlor was shown by Donaldson in 1977 (16) in which the peaks present within the spectrum were identified as specific functional groups that are present in Alachlor. An experimental spectrum can be seen above (Figure 4.6). The peaks identified were compared with the values shown by Donaldson and as can be seen the wavenumbers obtained were of similar values (Table 4.2).

Table 4.2: Comparison of wavenumbers from the literature (16) and experimental data with identification of bands. Experimental samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

Literature (cm^{-1})	Experimental (cm^{-1})	Identification
794	805	C-Cl
1066	1075	C-O-C
1457	1458	Aromatic C-C
1688	1698	C=O
2926	2907	Aliphatic C-H
3012	2981	Aromatic C-H

The wavelength selected to show the enrichment of alachlor was 1064 cm^{-1}, which can be attributed to the C-O ether stretch that is present in the molecule. In the figure below ten distinct times can be seen overlaid. This shows the increase in absorbance that was seen with increase in time (Figure 4.7).

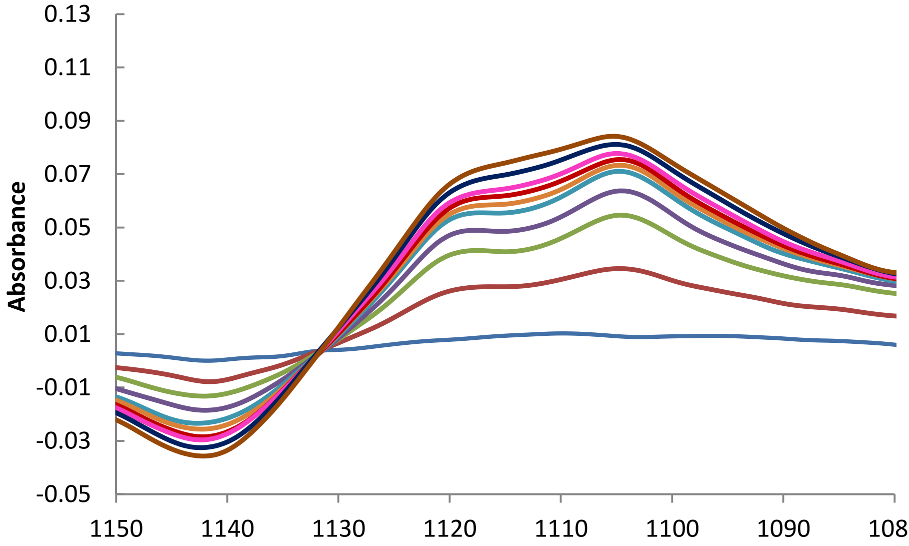

Figure 4.7: Overlay of IR spectra for alachlor. Spectra of alachlor diffusion into the passive sampling membrane is shown for a series of times (Initial: Blue; 17 min: wine; 50 min: green; 1.4 h: purple, 2.25 h: aqua blue; 2.75 h: orange; 3.25 h: red; 3.75 h: pink; 5.5 h: dark blue; 7.5 h: brown) Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

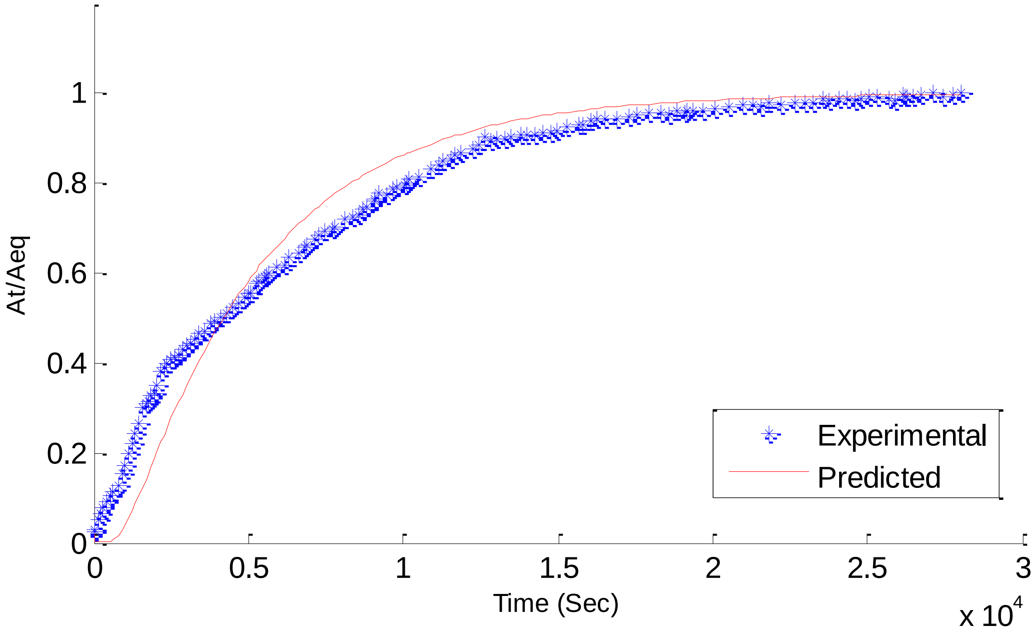

Figure 4.8: 100 mgL^{-1} Alachlor diffusion into a 44.22 µm plasticised polymeric membrane. Wavelength monitored 1064 cm^{-1} attributed to the C-O ether stretch present in the molecule. Both the experimental (*) and the predicted (-) values plots can be seen. Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

The absorbance at equilibrium was found to be 0.1058. T_{90} was reached after a period of 12467 sec (approx. 3.5 h). When the experimental data (sample time, absorbance of 1064 cm^{-1}, d_p: 0.000199 cm, L: 0.00442 cm) was inputted into the mathematical formula to calculate the diffusion coefficient the value obtained was 1.895 x 10^{-9} cm^{2}sec^{-1}. This value was then inputted into equation 4.6 to determine the predicted curve (red continuous line) using the previous time values (experimental).

4.3.5.2 ATRAZINE

IR spectra were obtained of atrazine diffusing into the novel plasticized membrane over a period of 8.75 h using the parameters mentioned previously (Table 4. 1).

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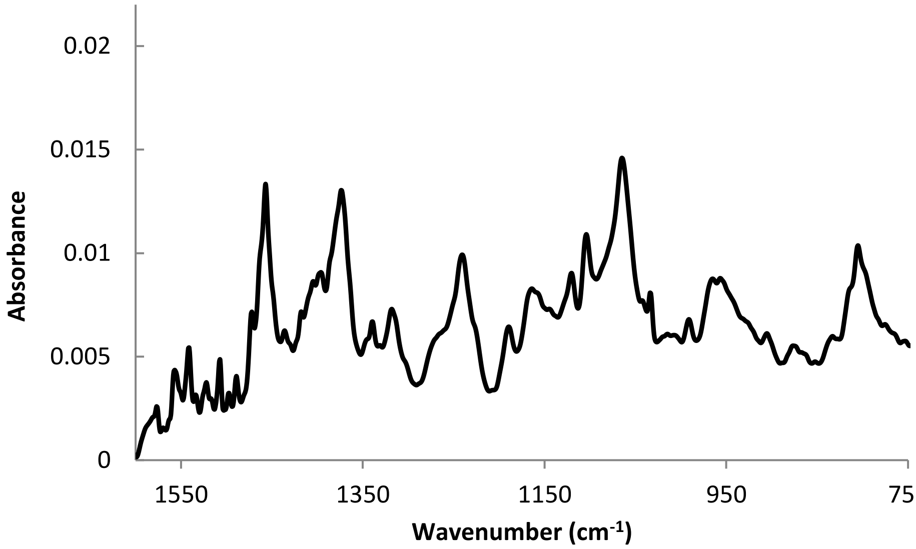

Figure 4.9: IR spectum obtained for atrazine. Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm-1, interval 1 cm-1, number of scans 4.

A spectrum of atrazine was obtained from Sigma Aldrich in which the peaks present within the spectrum were identified as specific functional groups that are present in atrazine. An experimental spectrum can be seen above (Figure 4.9). The peaks identified were compared with the values given by Sigma Aldrich and as can be seen (Table 4.3) the wavenumbers obtained were of similar values.

Table 4.3: Comparison of wavenumbers from the literature and experimental data with identification of bands. Experimental samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

Literature	Experimental	Identification
806	806	C-Cl stretch
1244	1242	in plane C-H bending
1304	1310	C-N stretch
1550	1541	C=C aromatic stretch

The wavelength selected to show the enrichment of atrazine was 1408 cm^{-1}, which can be attributed to –C-H bending that is present in the molecule (Figure 4.10)

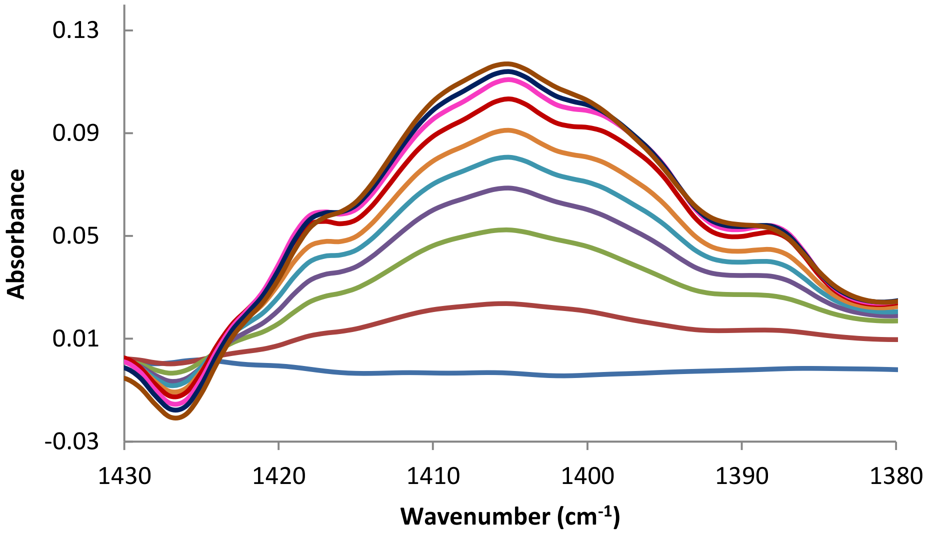

Figure 4.10: Overlay of IR spectra for atrazine. Spectra of atrazine diffusion into the passive sampling membrane is shown for a series of times (Initial: Blue; 11 min: wine; 1.1 h: green; 2.1 h: purple, 3 h: aqua blue; 4 h : orange; 5.3 h: red; 6.75 h: pink; 7.75 h: dark blue; 9.25 h: brown). Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

The absorbance at equilibrium was found to be 0.1102. T_{90} was reached after a period of 17962 sec (approx. 5 h) (Figure 4.11).

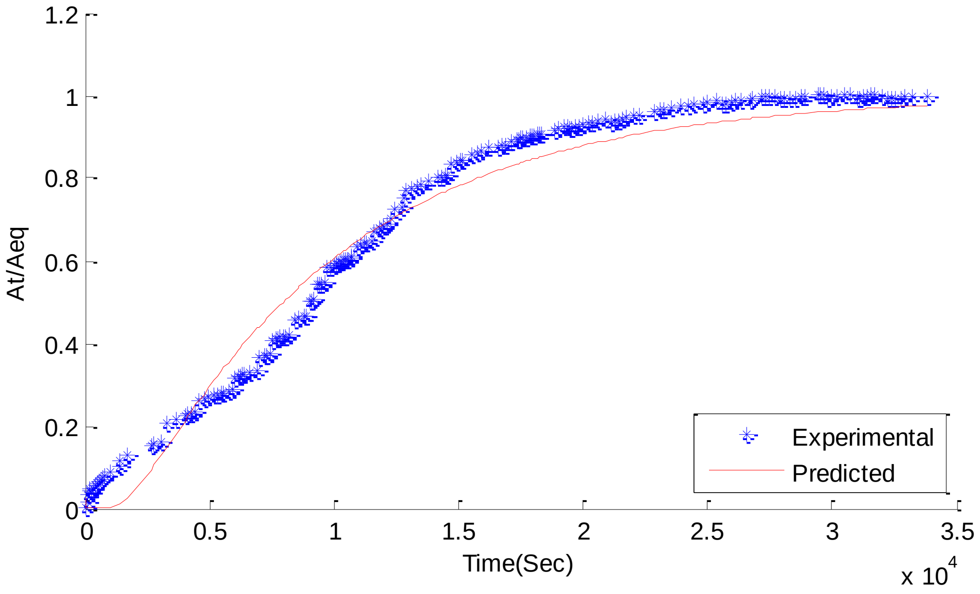

Figure 4.11: 100 mgL^{-1} Atrazine diffusion into a 44.22 µm Polymer membrane. Wavelength monitored 1408 cm^{-1} attributed to the –C-H bending (alkane) present in the molecule. Both the experimental (*) and the predicted (-) values plots can be seen. Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

When the experimental data (sample time, absorbance of 1408 cm^{-1}, d_p: 0.0001338 cm, L: 0.00442 cm) was inputted into the mathematical formula to calculate the diffusion coefficient the value obtained was 1.416 x 10^{-9} cm^{2}sec^{-1}. This value was then inputted into Equation 4.6 to determine the predicted curve (red continuous line) using the previous time values (experimental).

4.3.5.3 DIELDRIN

IR spectra were obtained of dieldrin diffusing into the novel plasticized membrane over a period of 1.7 h using the parameters mentioned previously (Table 4. 1)

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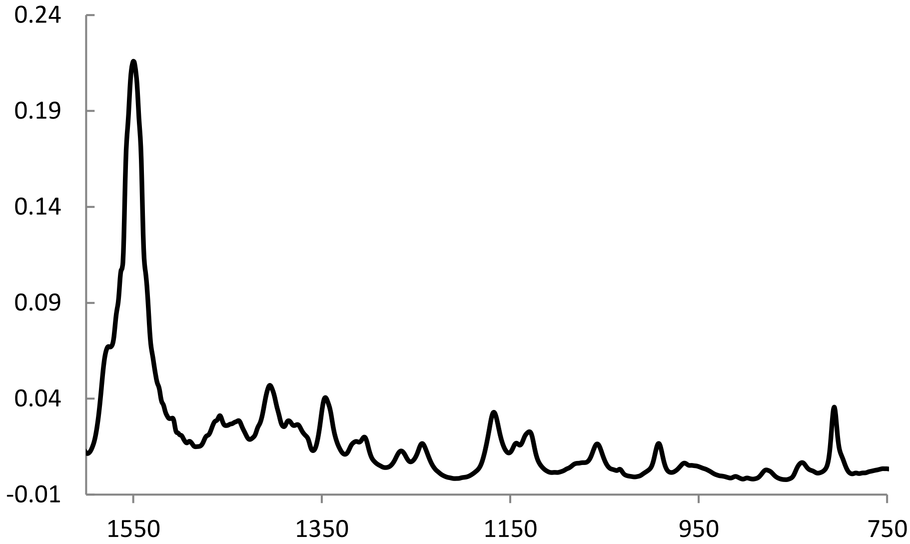


Figure 4.12: Ir spectum obtained for dieldrin. Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm-1, interval 1 cm-1, number of scans 4.

A spectrum of dieldrin was shown by Henderson *et al.* (17) in which the peaks present within the spectrum were identified as specific functional groups that are present in dieldrin. An experimental spectrum can be seen above (Figure 4.12). The peaks identified were compared with the values shown by Henderson *et al.* and as can be seen (Table 4.4) the wavenumbers obtained were of similar value.

Table 4.4: Comparison of wavenumbers from the literature (17) and experimental data with identification of bands. Experimental samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

Literature	Experimental	Identification
840	839	Epoxide group
1050	1058	C-C Skeleton vibration cyclohexane ring
1128	1130	C-O-C (saturated aliphatic ester)
1345	1346	C-H Bending
1439	1445	$-CH_2$ deformation

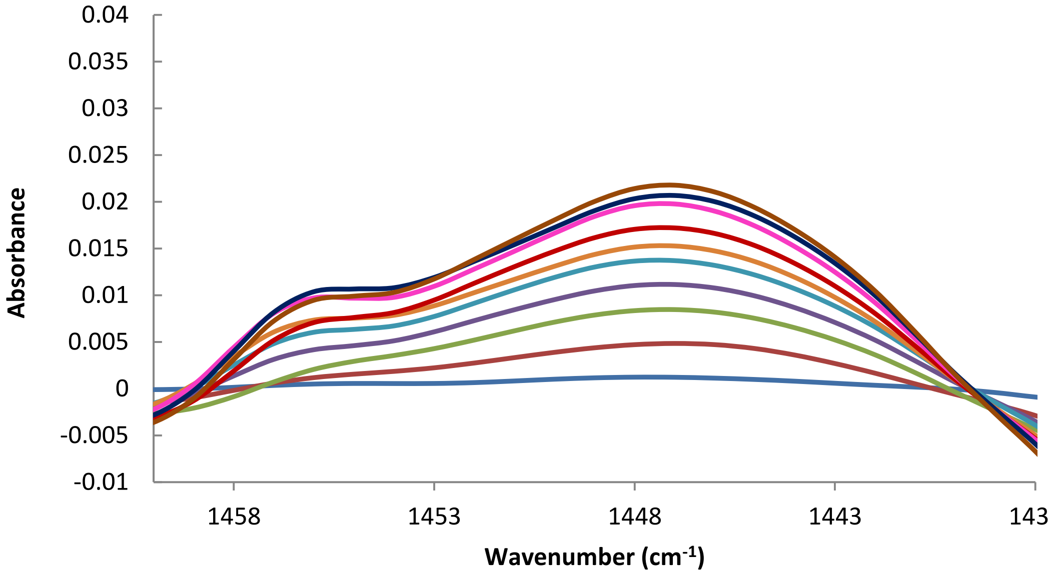


Figure 4.13: Overlay of IR spectra for dieldrin. The IR spectra of dieldrin neat (black) is shown alongside the spectra obtained during the diffusion of naphthalene into the passive sampling membrane. Spectra of dieldrin diffusion into the passive sampling membrane is shown for a series of times (Initial: Blue; 5 min: wine; 13 min: green; 20 min: purple, 31 min: aqua blue; 40 min : orange; 55 min: red; 72 min: pink; 85 min: dark blue; 98 min: brown). Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

The wavelength selected to show the enrichment of atrazine was 1447 cm^{-1}, which can be attributed to –CH_2 deformation that is present in the molecule (Figure 4.13)

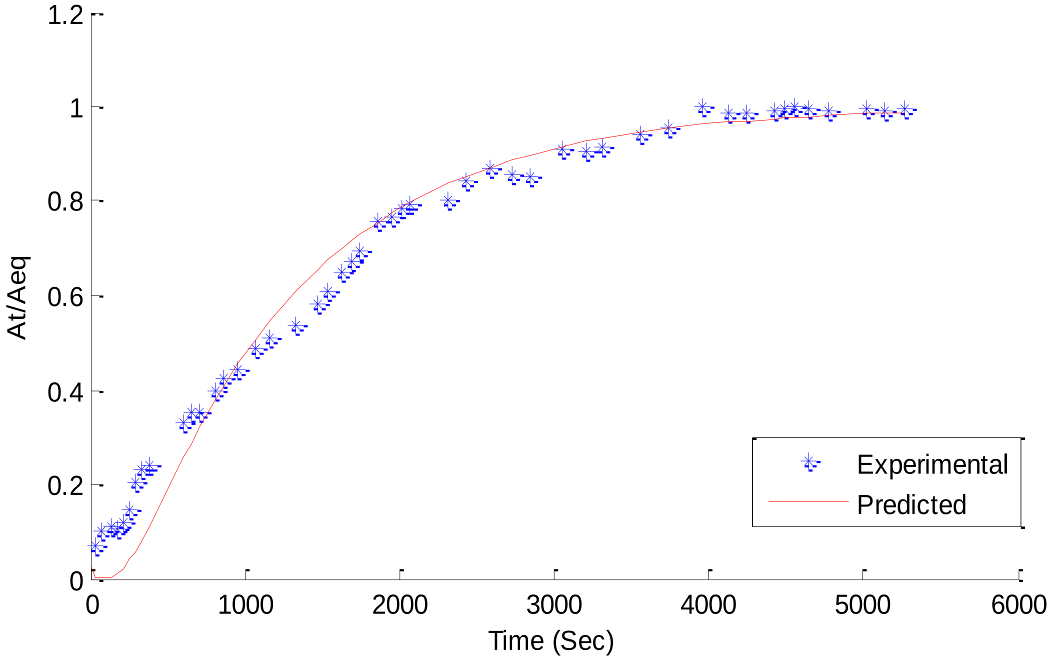


Figure 4.14: 100 mgL^{-1} Dieldrin diffusion into a 44.22 µm Polymer membrane. Wavelength monitored 1447 cm^{-1} attributed to the –CH2 deformation present in the molecule. Both the experimental (*) and the predicted (-) values plots can be seen. Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

The absorbance at equilibrium was found to be 0.3069. T_{90} was reached after a period of 4246 sec (approx. 1.2 h). When the experimental data (sample time, absorbance of 1447 cm^{-1}, d_p: 0.000156 cm, L: 0.00442 cm) was inputted into the mathematical formula to calculate the diffusion coefficient the value obtained was 5.898 x 10^{-9} cm^{2}sec^{-1}. This value was then inputted into Equation 4.6 to determine the predicted curve (red continuous line) using the previous time values.

4.3.5.4 NAPHTHALENE

IR spectra were obtained of naphthalene diffusing into the novel plasticized membrane over a period of 5.9 h using the parameters mentioned previously (Table 4. 1).

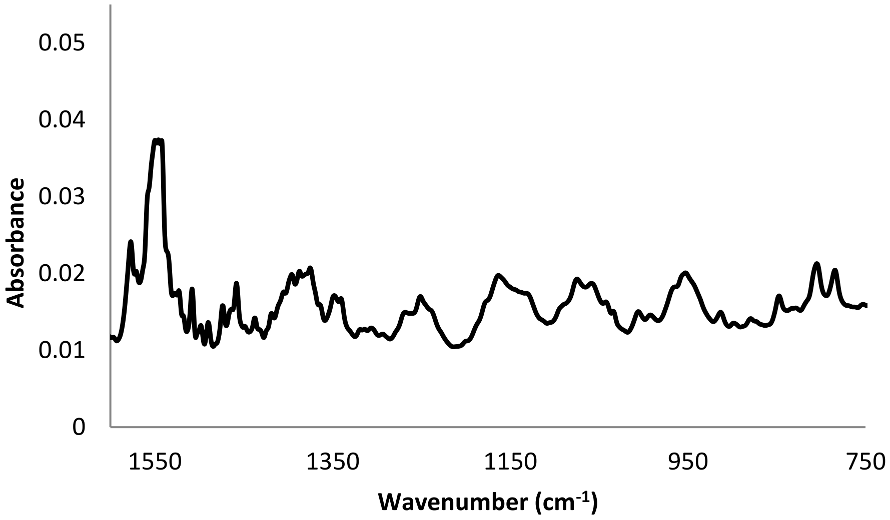


Figure 4.15: Ir spectum obtained for naphthalene. Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm-1, interval 1 cm-1, number of scans 4.

A spectrum of naphthalene was shown by Pimentel *et al.* (18) in which the peaks present within the spectrum were identified as specific functional groups that are present in naphthalene. An experimental spectrum can be seen above (Figure 4.15). The peaks identified were compared with the values shown by Pimentel *et al.* and as can be seen the wavenumbers obtained were of similar values (Table 4.5).

Table 4.5: Comparison of wavenumbers from the literature (18) and experimental data with identification of bands. Experimental samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

Literature	Experimental	Identification
779	789	-CH out of plane stretching
1012	1007	In plane C-H bending
1085	1075	In plane C-H bending
1548	1551	C-C stretches in the aromatic ring

The wavelength selected to show the enrichment of naphthalene was 789 cm^{-1}, which can be attributed to –C-H out of plane stretching that is present in the molecule (Figure 4.16).

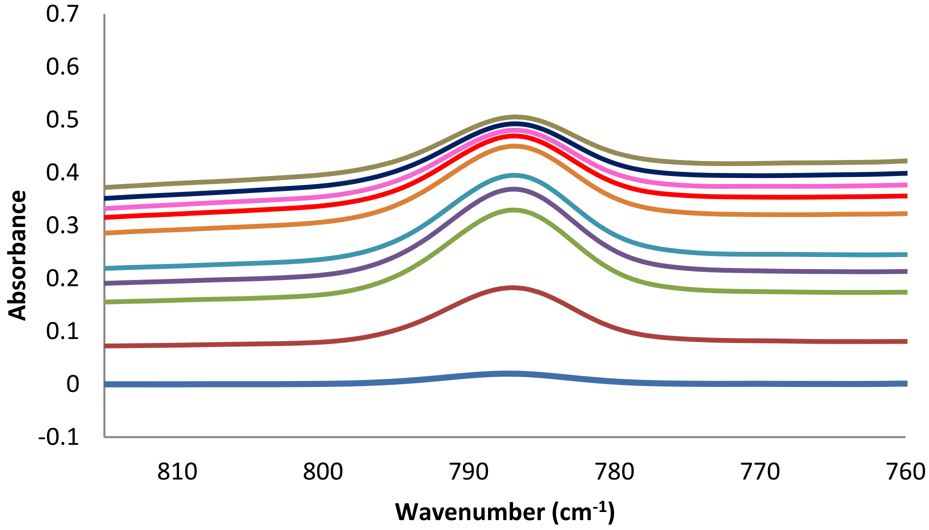


Figure 4.16: Overlay of IR spectra for naphthalene. Spectra of naphthalene diffusion into the passive sampling membrane is shown for a series of times (Initial: Blue; 5 min: wine; 30 min: green; 51 min: purple, 1.25 h: aqua blue; 2.6 h : orange; 3.3 h: red; 4.2 h: pink; 5 h: dark blue; 5.9 h: brown). Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

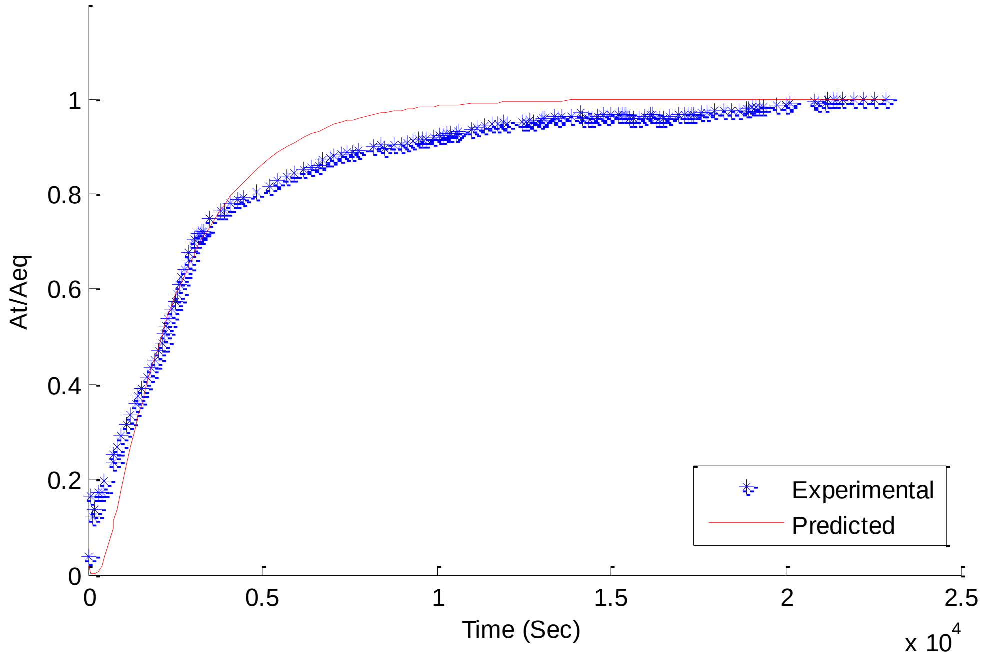


Figure 4.17: 100 mgL^{-1} Naphthalene diffusion into a 44.22 µm Polymer membrane. Wavelength monitored 789 cm^{-1} attributed to the –CH out of plane stretching present in the molecule. Both the experimental (*) and the predicted (-) values plots can be seen. Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

The absorbance at equilibrium was found to be 0.5190. T_{90} was reached after a period of 8771 sec (approx. 2.4 h). When the experimental data (sample time, absorbance of 789 cm^{-1}, d_p: 0.000269 cm, L: 0.00442 cm) was inputted into the mathematical formula to calculate the diffusion coefficient and the value obtained was 3.5352 x 10^{-9} cm^2sec^{-1}. This value was then inputted into Equation .4.6 to determine the predicted curve (red continuous line) using the previous time values.

4.3.5.5 ALDRIN

IR spectra were obtained of aldrin diffusing into the novel plasticized membrane over a period of 3 h using the parameters mentioned previously (Table 4. 1)

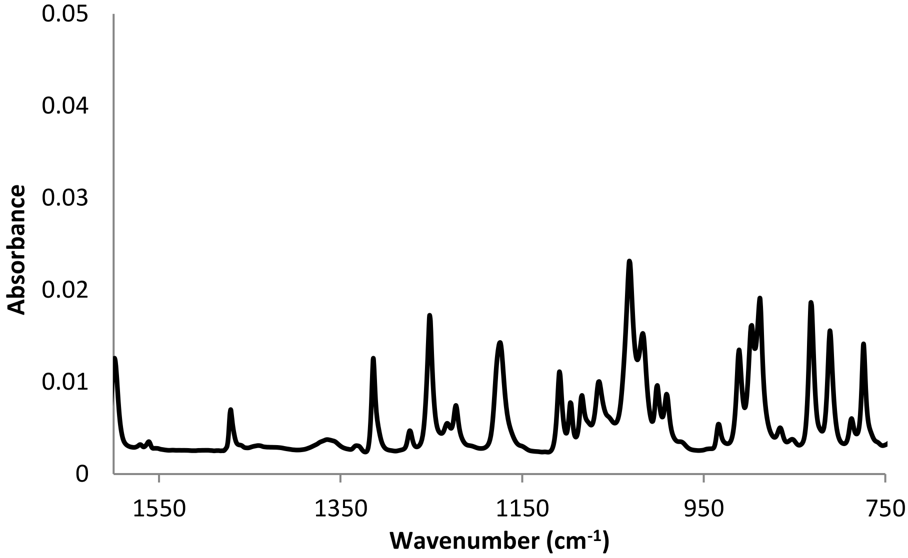


Figure 4.18: Ir spectum obtained for aldrin Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm-1, interval 1 cm-1, number of scans 4.

A spectrum of aldrin was shown by Bourne *et al.* (19) in which the peaks present within the spectrum were identified as specific functional groups that are present in aldrin. An experimental spectrum can be seen above (Figure 4.18). The peaks identified were compared with the values shown by Bourne *et al.* and as can be seen the wavenumbers obtained were of similar values (Table 4.6).

Table 4.6: Comparison of wavenumbers from the literature (19) and experimental data with identification of bands for aldrin. Experimental samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm-1, interval 1 cm-1, number of scans 4.

Literature	Experimental	Identification
773	774	C-Cl Stretch
1067	1065	C-O Ether stretch
1249	1252	C-N stretch
1314	1314	C-N stretch
1469	1471	Aromatic C=C bonds

The wavelength selected to show the enrichment of aldrin was 1018 cm^{-1}, which can be attributed to =C-H bending that is present in the molecule (Figure 4.19).

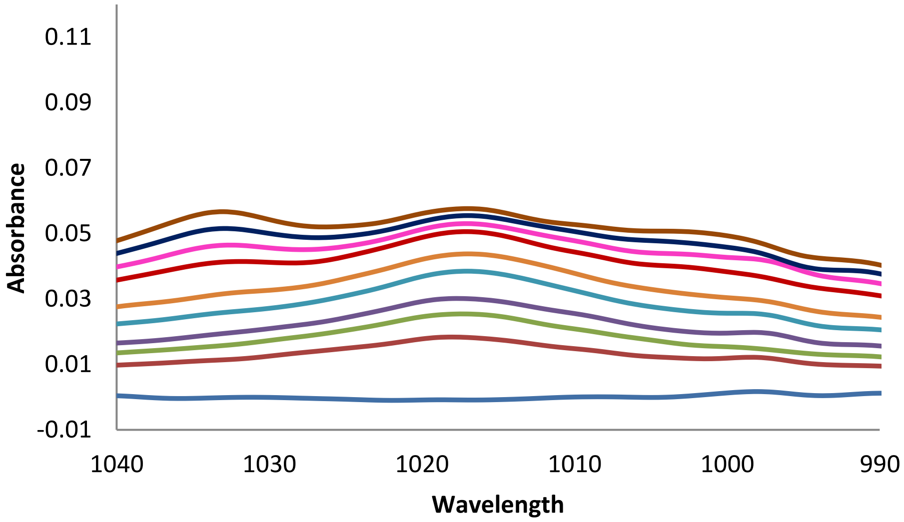


Figure 4.19: Overlay of IR spectra for aldrin. Spectra of aldrin diffusion into the passive sampling membrane is shown for a series of times (Initial: Blue; 5 min: wine; 13 min: green; 20 min: purple, 31 min: aqua blue; 40 min : orange; 55 min: red; 72 min: pink; 85 min: dark blue; 98 min: brown). Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

The absorbance at equilibrium was found to be 0.4066. T_{90} was reached after a period of 6882 sec (approx. 1.9 h). When the experimental data (sample time, absorbance of 789 cm^{-1}, d_p: 0.000208 cm, L: 0.00442 cm) was inputted into the mathematical formula to calculate the diffusion coefficient the value obtained was 3.125 x 10^{-9} cm^{2}sec^{-1}. This value was then inputted into Equation 4.6 to determine the predicted curve (red continuous line) using the previous time values (experimental).

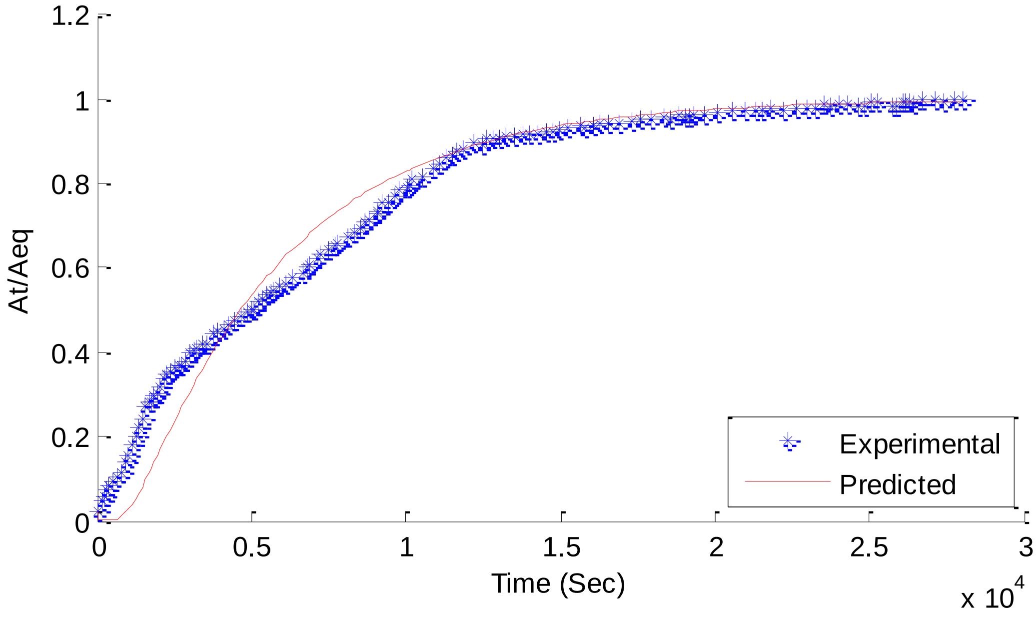


Figure 4.20: 100 mgL^{-1} Aldrin diffusion into a 44.22 µm Polymer membrane. Wavelength monitored 1018 cm^{-1} attributed to the =C-H bending present in the molecule. Both the experimental (*) and the predicted (-) values plots can be seen. Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

4.3.5.6 BENZO (K) FLUORANTHENE

IR spectra were obtained of benzo (k) fluoranthene diffusing into the novel plasticized membrane over a period of 2.2 h using the parameters mentioned previously (Table 4. 1)

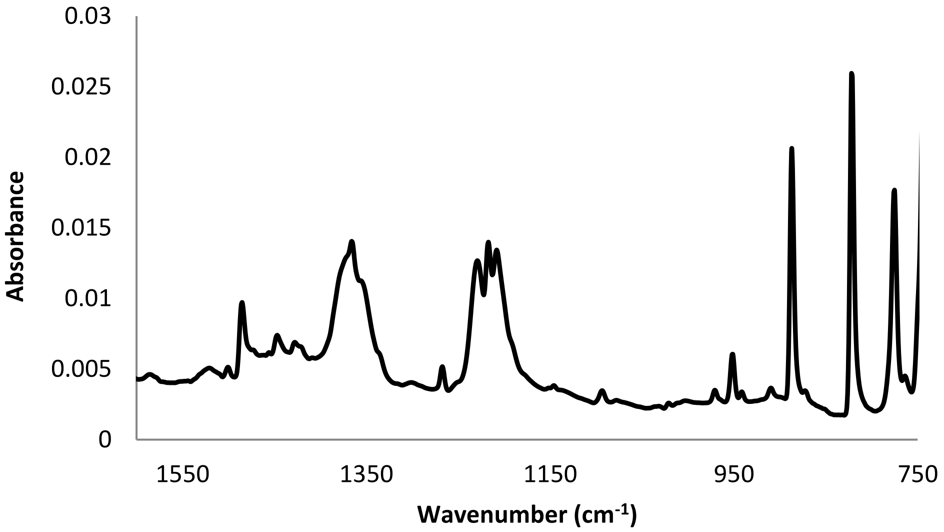


Figure 4.21: Ir spectum obtained for benzo (k) fluoranthene Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm-1, interval 1 cm-1, number of scans 4.

A spectrum of benzo (k) fluoranthene was shown by Hudgins *et al.* (20) which the peaks present within the spectrum were identified as specific functional groups that are present in benzo (k) fluoranthene. An experimental spectrum can be seen above (Figure 4.21). The peaks identified were compared with the values shown by Hudgens *et al.* and as can be seen the wavenumbers obtained were of similar values (Table 4.7).

Table 4.7: Comparison of wavenumbers from the literature (20) and experimental data with identification of bands. Experimental samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

Literature	Experimental	Identification
773	775	C-H out of plane stretch
823	822	C-H out of plane stretch
883	887	C-H out of plane stretch
1207	1207	in plane C-H bending
1266	1267	in plane C-H bending
1451	1445	C-C in ring stretch

The wavelength selected to show the enrichment of benzo (k) fluoranthene was 1405 cm^{-1}, which can be attributed to –C-H bending that is present in the molecule (Figure 4.22).

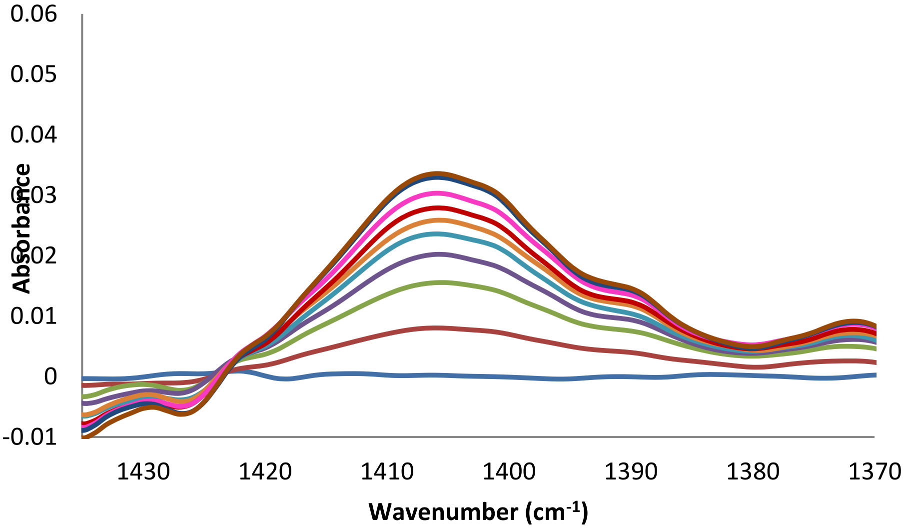


Figure 4.22: Overlay of IR spectra for benzo (k) fluoranthene. Spectra of benzo (k) fluoranthene diffusion into the passive sampling membrane is shown for a series of times (Initial: Blue; 4 min: wine; 16 min: green; 28 min: purple, 42 min: aqua blue; 52 min : orange; 1 h : red; 1.3 h min: pink; 1.6 h min: dark blue; 2 h min: brown). Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

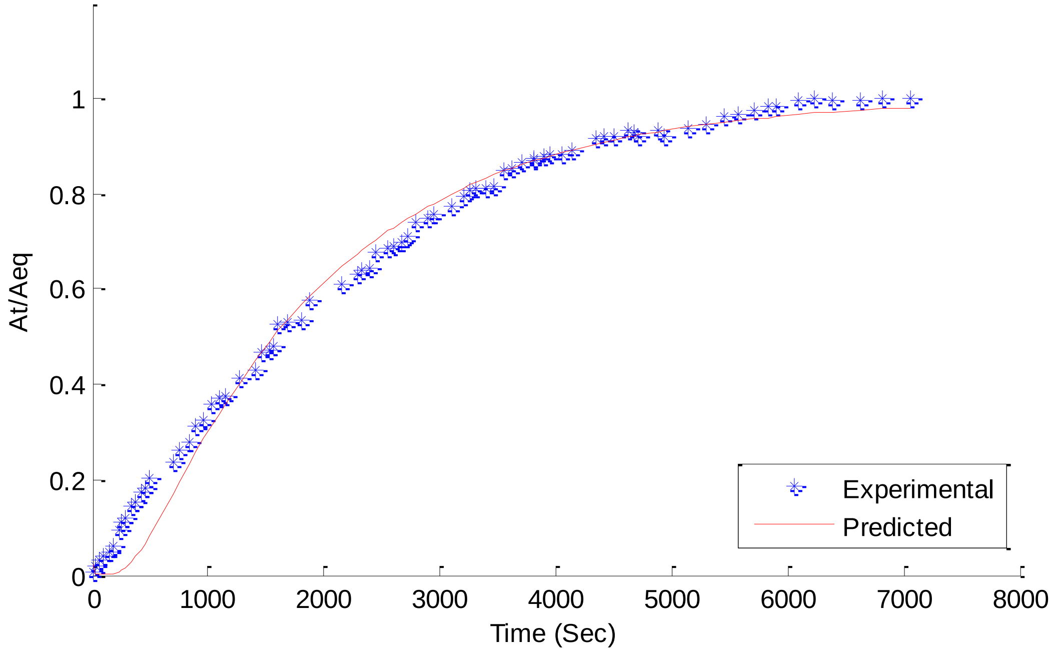


Figure 4.23: 100 mgL^{-1} Benzo (k) fluoranthene diffusion into a 44.22 µm Polymer membrane. Wavelength monitored 1405 cm^{-1} attributed to the C-H bending present in the aromatic ring of the molecule. Both the experimental (*) and the predicted (-) values plots can be seen. Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

The absorbance at equilibrium was found to be 0.0361. T_{90} was reached after a period of 4143 sec (approx. 1.15 h). When the experimental data (sample time, absorbance of 1405 cm^{-1}, d_p: 0.000151 cm, L: 0.00442 cm) was inputted into the mathematical formula to calculate the diffusion coefficient the value obtained was 4.7266 x 10^{-9} cm^{2}sec^{-1}. This value was then inputted into Equation 4.6 to determine the predicted curve (red continuous line) using the previous time values (experimental).

4.3.6 MODELLING OF RESULTS

4.3.6.1 T_{90} AND T_{100}

There are two times of great significance when determining the diffusion of an analyte. These two terms are T_{90} and T_{100}. The T_{90} is the time at which the 90% of the maximum absorbance is reached. T_{100} is the time in which 100% of the maximum absorbance of the analyte is reached. These terms are useful in the study of diffusion of penetrants into a passive sampling membrane as they can aid in the determination of the kinetic regime. As shown previously within a Fickian diffusion curve you have two regions, kinetic and equilibrium (Figure 4.5). Depending on the passive sampler type (Chapter 1, Section 1.4.3) one would wish to deploy it is important to know when the sampler has reached equilibrium.

When looking at the diffusion profiles for the above six values, the T_{90} and T_{100} values were calculated (Section 4.3.5). It was then determined to plot these values against the Log K_{ow} of the compounds to determine if any correlation could be determined. As can be seen from the following graph, these correlations followed a polynomial trend in both cases , with the best fit line showing r^2 values of 0.9817 and 0.9417 respectively (Figure 4.24).

Table 4.8: Compounds tested experimentally to calculate models for prediction of T_{90} and T_{100}. Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

		T_{90}		T_{100}	
Compound	Log K_{ow}	Time (min)	Abs	Time (min)	Abs
Atrazine	2.61	351	0.0993	520	0.1104
Naphthalene	3.3	268	0.4671	351	0.5190
Alachlor	3.5	299	0.0952	451	0.1058
Dieldrin	5.4	55	0.0170	65	0.0189
Benzo k fluoranthene	5.6	49	0.0294	99	0.0334
Aldrin	6.1	111	0.0517	164	0.0574

Six compounds were tested experimentally to calculate their T_{90} and T_{100} values. These compounds with the experimental values are seen above (Table 4. 1). The values for T_{90} and T^{100} were plotted against the Log K_{ow} values for the compounds. In both cases a third order polynomial relationship was seen.

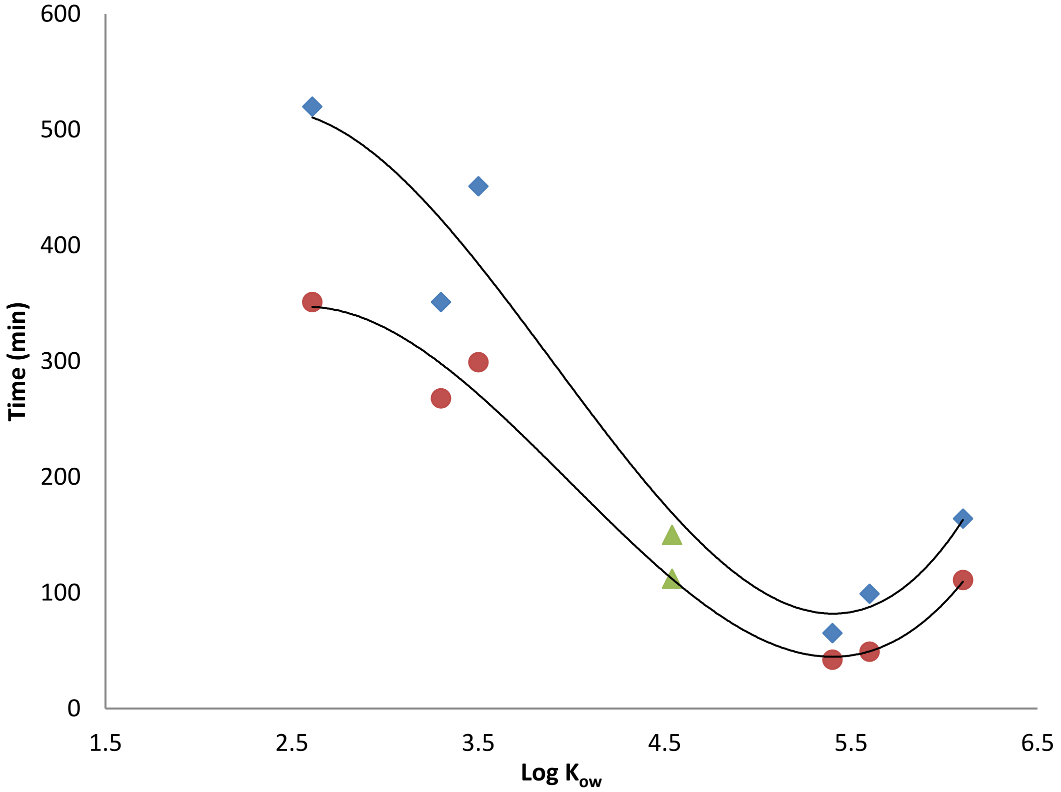


Figure 4.24: Model showing the prediction of both T_{90} (O) and T_{100} (◊) over a Log K_{ow} range of 2.6 to 6.1. The equation of the line and r^2 value for both series were determined (T_{90}: $26.896x^3 - 321.94x^2 + 1123.8x - 871.37$ ($R^2 = 0.9817$); T_{100}: $32.024x^3 - 374.69x^2 + 1244.3x - 754.02$ (R^2: 0.9451)). A third series (Anthracene (Δ)) is also shown with experimental values for T_{90} and T_{100} that were not used in the establishment of the model. Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

As can be seen for both the T_{90} and T_{100} plots third order polynomial curves were determined with good correlation (0.9817 and 0.9451 respectively) (Figure 4.3). The compounds mentioned above were used to establish the prediction curve (Table

4.8), and then a seventh compound, anthracene, was used to establish the accuracy of the curves in relation to prediction values for both T_{90} and T_{100} values.

Anthracene was run under the same conditions as the previous 6 compounds, 100 mgL^{-1} diffusing into a 44.22 µm novel polymeric membrane and analysed using the ATR conditions previously outlined (Table 4. 1). The values determined experimentally for T_{90} and T_{100} were inputted in to the predicted model to test the accuracy of the model. As can be seen the two values calculated for anthracene fell within the curve for both T_{90} and T_{100} with % RSD being calculated within 7.4% and 13.1% respectively (Figure 4.24).

As with previous pollutants the experimental data obtained (time and At/Aeq) were inputted into the Matlab script to calculate D (diffusion coefficient). The diffusion coefficient in turn was used to calculate the predicted values of A_t/A_{eq} and these two graphs are shown overlaid to demonstrate the correlation obtained.

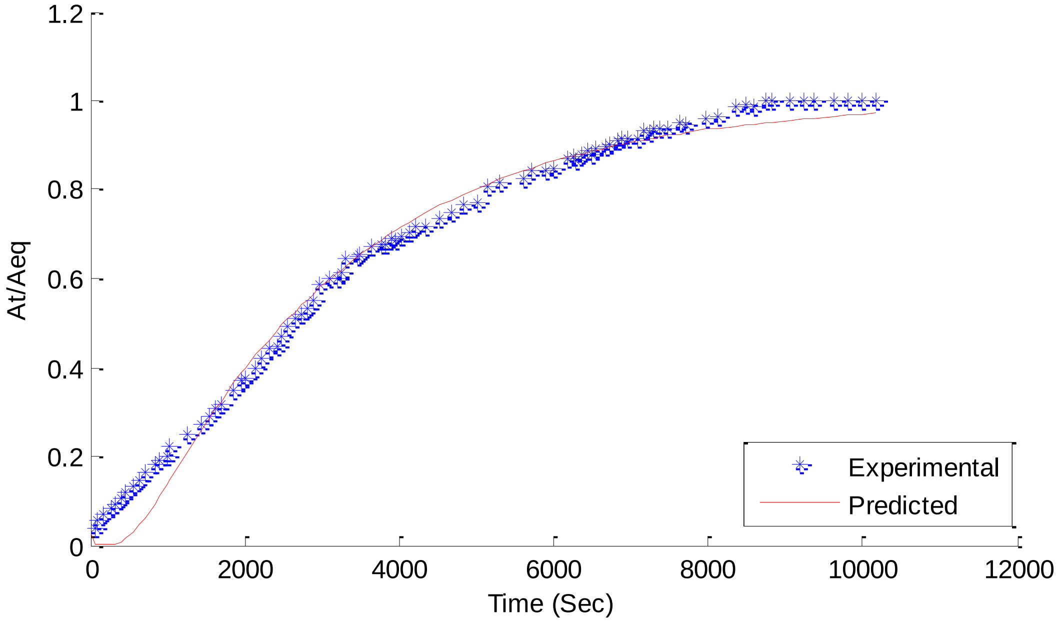


Figure 4.25: Enrichment curves of anthracene diffusion into diisononyl adipate membrane (15% PVC (W/V), 50% Plasticiser (w/w) 100 ul) Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

The wavelength selected to show the enrichment of anthracene was 1540 cm^{-1}. The absorbance at equilibrium was found to be 0.1104. T_{90} was reached after a period of 6736 sec (approx. 1.9 h) (Figure 4.25). When the experimental data (sample time, absorbance of 1540 cm^{-1}, d_p: 0.000138 cm, L: 0.00442 cm) was inputted into the mathematical formula to calculate the diffusion coefficient the value obtained was 2.9492 x 10^{-9} cm^{2}sec^{-1}. This value was then inputted into Equation 4.6 to determine the predicted curve (red continuous line) using the previous time values. From the equation of the line determined for both T_{90} and T_{100} (Figure 4.24) predicted values for both of these times were calculated. For the seven compounds for which these values were experimentally calculated the % RSD of the difference is shown alongside the experimental values (Table 4.9).

Table 4.9: Predicted T_{90} and T_{100} for priority pollutants based on Log K_{ow}. Also shown is experimental values obtained and the % RSD from predicted. Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

		Predicted		Experimental	
CAS number	***Name of priority substance***	T_{90} (min)	T_{100} (min)	T_{90} (min)	T_{100} (min)
15972-60-8	Alachlor	271.3	384.1	306 ± 8.5%	451 ± 11.3%
1912-24-9	Atrazine	346.9	510.6	351 ± 0.8%	520 ± 1.3%
470-90-6	Chlorfenvinphos	222.9	316.7		
2921-88-2	Chlorpyrifos	46.4	84.3		
117-81-7	Di(2-ethylhexyl)phthalate (DEHP)	794.8	1012.0		
330-54-1	Diuron	346.0	506.7		
115-29-7	Endosulfan	271.3	384.1		
959-98-8	(alpha-endosulfan)	221.3	314.5		
118-74-1	Hexachlorobenzene	45.5	83.1		
87-68-3	Hexachlorobutadiene	82.0	130.2		
608-73-1	Hexachlorocyclohexane (alpha)	226.1	321.0		
	Hexachlorocyclohexane (beta)	229.2	325.3		
	Hexachlorocyclohexane	171.7	247.7		

	delta				
58-89-9	(gamma-isomer, Lindane)	210.2	299.3		
34123-59-6	Isoproturon	339.7	491.2		
104-40-5	(4-(para)-nonylphenol)	60.4	101.7		
1806-26-4	Octylphenols	51.8	91.3		
140-66-9	(para-tert-octylphenol)	241.7	342.5		
608-93-5	Pentachlorobenzene	50.3	89.3		
87-86-5	Pentachlorophenol	48.9	87.6		
122-34-9	Simazine	343.2	516.8		
50-29-3	para-para-DDT	172.9	242.1		
309-00-2	Aldrin	109.3	162.8	111±1.1%	164 ± 0.5%
60-57-1	Dieldrin	44.5	81.9	42 ± 4.1%	65 ± 16.2%
72-20-8	Endrin	48.9	87.6		
465-73-6	Isodrin	45.3	82.8		
1582-09-8	Trifluralin	45.5	83.1		
120-12-7	Anthracene	111.8	168.8	112 ± 0.1%	150 ±8.4%
206-44-0	Fluoranthene (****)	91.3	142.1		
91-20-3	Naphthalene	297.8	422.6	268 ± 7.4%	351 ± 13.1%
50-32-8	(Benzo(a)pyrene),	86.3	134.1		
205-99-2	(Benzo(b)fluoranthene),	62.3	104.1		
191-24-2	(Benzo(g,h,i)perylene),	266.4	358.4		
207-08-9	(Benzo(k)fluoranthene) C18	49.2	87.7	49 ± 0.3%	99 ± 8.6%
	(Benzo(k)fluoranthene), C20	111.3	165.3		
193-39-5	(Indeno(1,2,3-cd)pyrene) $C_{22}H_{11}$	340.9	450.9		
	(Indeno(1,2,3-cd)pyrene) $C_{22}H_{12}$	517.5	669.6		
71-43-2	Benzene	321.6	505.9		
107-06-2	1,2 - Dichloroethane	173.9	370.6		
75-09-2	Dichloromethane	104.6	300.7		
120-82-1	(1,2,4-Trichlorobenzene)	190.9	273.4		
67-66-3	Trichloromethane (Chloroform)	298.7	488.0		
56-23-5	Carbontetrachloride	340.2	492.3		
127-18-4	Tetrachloroethylene	285.0	403.9		
79-01-6	Trichloroethylene	336.8	515.1		

4.3.6.2 DIFFUSION COEFFICIENT

The calculated diffusion coefficients for the priority pollutants diffusing into the passive sampling membranes are shown below (Table 4.10). These values were calculated using a script written for Matlab (Appendix I) which calculated the diffusion coefficient using Equation 4.6.

Table 4.10: Diffusion coefficients (cm^2s^{-1}) for the analytes diffusing in the novel plasticised membranes calculated by the Matlab model. Log Kow values are also supplied for each of the pollutants

	Log K_{ow}	D (cm^2s^{-1})
Atrazine	2.61	1.42×10^{-9}
Aldrin	6.1	3.13×10^{-9}
Alachlor	3.5	1.90×10^{-9}
Anthracene	4.54	2.95×10^{-9}
Naphthalene	3.3	3.54×10^{-9}
Benzo k fluoranthene	5.6	4.73×10^{-9}
Dieldrin	5.4	5.90×10^{-9}

Through review of the trend in Log K_{ow} for the compounds no correlation between the pollutant Log K_{ow} and pollutant diffusion coefficient is seen (Figure 4.26).

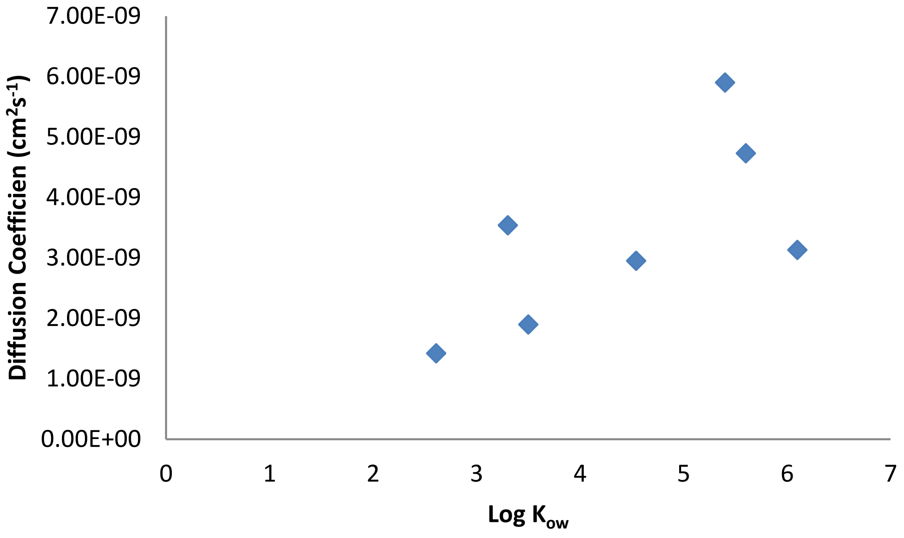


Figure 4.26: Diffusion coeffiencts calculated for penetrents plotted against their Log K_{ow} values. As can be shown no trend can be observed.

This could suggest that the difference in the diffusion coefficient is not down to the water solubility of the compound but is also affected by steric/molecular size effects. This effect has been reported previously within the literature (21). It was reported that the diffusion coefficients decrease with increasing molecular size, and as the diffusant size becomes larger, the decrease in D with increasing molar volume becomes less pronounced. From looking at the values of D obtained from experimental results in this work, it was seen that increase in molecular weight and molecular size did not lead to a steady decrease in D values.

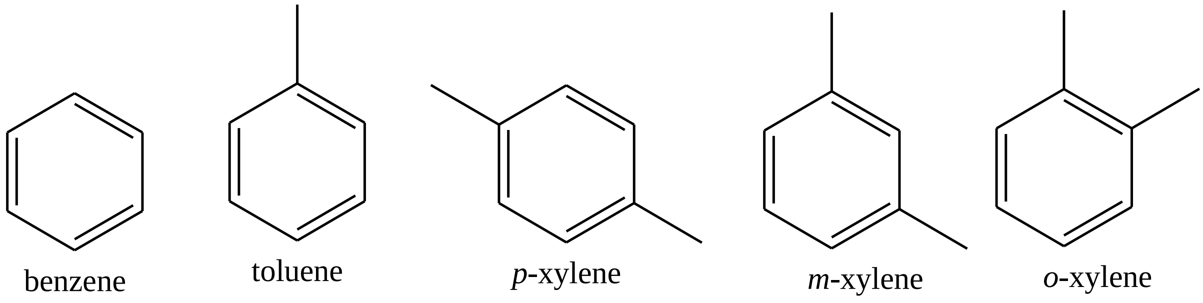


Figure 4.27: Structures of the BTEX compounds studied by Salem *et al.* (22) in a study to investigate the effect of the shape and size of the penetrant molecule on diffusion coefficient values.

A study was carried out by Saleem *et al.* (22) in order to investigate the effect of the shape and size of the penetrant molecules on their diffusion coefficient. It was found that the shape of the penetrants had a profound effect on diffusion into the polymer membrane. Penetrats that were linear, flexible and more symmetrical had higher mobility that rigid molecules. It was shown that with the addition of methyl groups to benzene the diffusion coefficient was reduced (benzene>toluene>p xylene>m xylene>o xylene (Structures can be seen in Figure 4.27). This showed that for the diffusion of these analytes into a LDPE film, the steric effects of molecule affected the rate of diffusion. When the diffusion coefficients of the same chemicals were studied for their diffusion into HDPE films (23) the addition of methyl groups did not affect the values obtained in the same way. This time the diffusion rates were found to be most rapid for toluene, followed by benzene and finally xylene. It was also found that though the HDPE film was thicker than the LDPE film (1 mm and 0.15 respectively) the diffusion coefficients were higher for the compounds tested in common. This illustrated that the diffusion coefficient is not only affected by the shape or size of the molecule but also the properties of the polymer membrane.

The range of diffusion coefficients obtained ($1.416 \times 10^{-9} – 7.03 \times 10^{-9}$ cm^2sec^{-1}) falls within the range of values previously reported for organic molecules of similar shape, size and polarity (22) (23).

4.3.7 ENRICHMENT OF MULTIPLE ANALYTES

The enrichment of single analytes into the passive sampling membrane has been shown previously (Section 4.3.1).In order to analyse the diffusion behaviour of a system with more than one component present, it is necessary to discern the effect of one component on the diffusion of the other. Due to complex effects that can be found in multicomponent systems it is important to quantify these effects. This is important for aquatic deployment of passive sampling devices as there will be more than one pollutant present in the surface water. For this reason it is of utmost importance to understand the difference that will occur between single and multi-component systems.

Three studies were carried out to determine the effect of multi component systems and are detailed below.

4.3.7.1 ATRAZINE AND DIELDRIN

It can be seen for both the diffusion of dieldrin and atrazine (Figure 4.28 and Figure 4.29 respectively) within a multi-component system there was an increase in time it took for the pollutant to reach T_{90} (7003 sec to 129090 sec) and with this there was also a decrease in the max absorbance determined for the compound. For dieldrin there was a 16% decrease in absorbance at T_{100} (0.3069 decreased to 0.2581) (Figure 4.28)

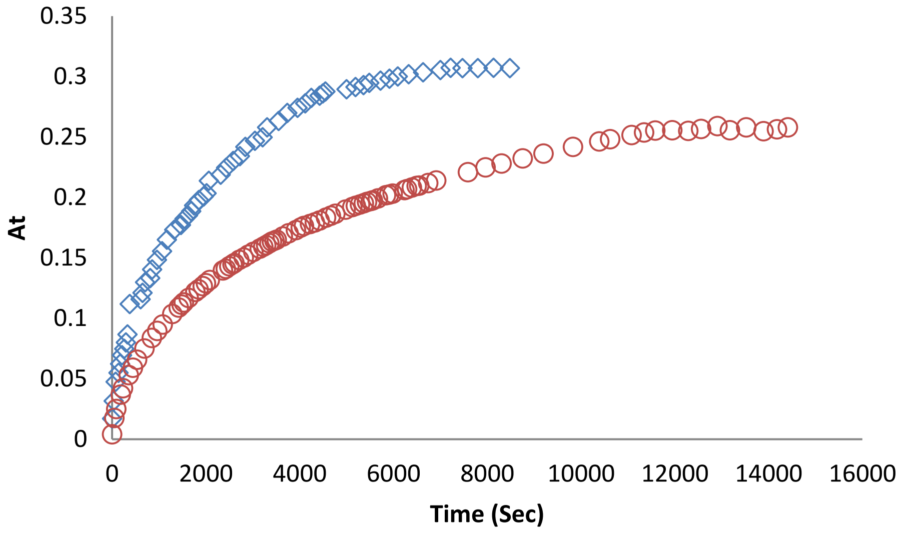


Figure 4.28: Enrichment curves of dieldrin (100 mgL^{-1}) singly (◊) and in a mixture with atrazine (O) into a 44.22 µm passive sampling membrane. A decrease in equilibrium absorbance can be observed alongside an increase in time taken to reach T_{100}. Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

In the case of dieldrin T_{90} was reached after a period of 4246 sec when the analyte was determined singly.When dieldrin was analysed within the multi component system a longer time period (8757 sec) was needed T_{90} to be reached (Figure 4.28)..

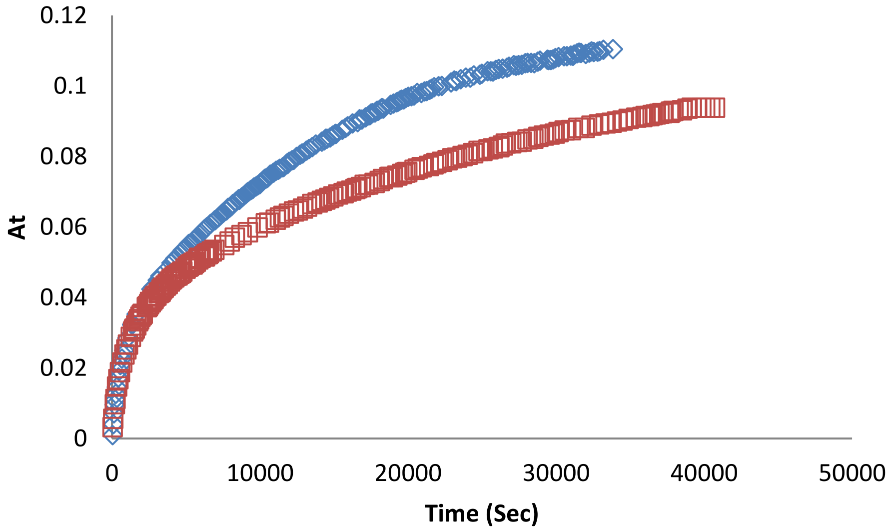


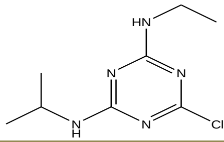
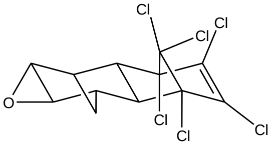
Figure 4.29: Enrichment curves of atrazine (100 mgL^{-1}) singly (◊) and in a mixture with atrazine (O) into a 44.22 µm passive sampling membrane. A decrease in equilibrium

absorbance can be observed alongside an increase in time taken to reach T_{100}. Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

The same trend as with dieldrin was noticed when looking at the diffusion of atrazine into the plasticized membrane. A decrease in absorbance at T_{100} was noted from 0.1102 to 0.0957. The increase in time it took to reach T_{90} was from 22073 to 27692 sec (Figure 2.29).

The experimental data obtained was inputted into the script written for Matlab in order to determine the diffusion coefficient for atrazine and dieldrin were calculated.

Table 4.11: 100 mgL^{-1} atrazine-dieldrin (single and multi component) diffusing into a 44.22 um plasticised PVC film. Diffusion coefficients and absorbance at T_{100} also given

		Diffusion Coefficient (cm^2sec^{-1})		Absorbance at T_{100}	
Analyte	Structure	Single Component	Multi Component	Single Component	Multi Component
Atrazine		1.416 x 10^{-9}	1.123 x 10^{-9}	0.1102	0.0937
Dieldrin		5.898 x 10^{-9}	3.047 x 10^{-9}	0.3069	0.2581

As can be seen within the multi component system the diffusion coefficient of the penetrant decrease with the presence of a second competing penetrant (Table 4.11). These results follow on from previous enrichment studies of atrazine and dieldrin (Section 3.3.3.4) where the concentration of dieldrin at equilibrium was found to be greater than that of atrazine. This also was seen when looking at the preconcentration factor of analytes into different passive sampling membranes (Table 3.6)

4.3.7.2 ALACHLOR AND DIELDRIN

As with the previous multi component system (Figure 4.3.6.1), when a second competing penetrant was entered into the system, a decrease in max absorbance was noted with an increase in the length of time to reach T_{90}.

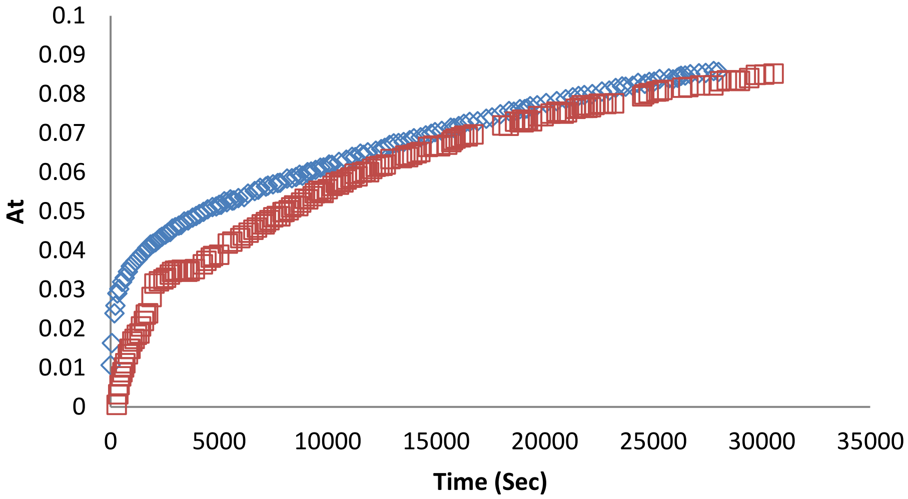


Figure 4.30: Enrichment curves of alachlor (100 mgL^{-1}) singly (◊) and in a mixture with dieldrin (O) into a 44.22 µm passive sampling membranes. Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

In the case of alachlor the decrease in the max absorbance was minute (0.0860 in single systems decreased to 0.0852 in multi component system). The increase in time taken to reach equilibrium was also minimal (21712 to 22136 sec for single and multi component system respectively) (Figure 4.30).

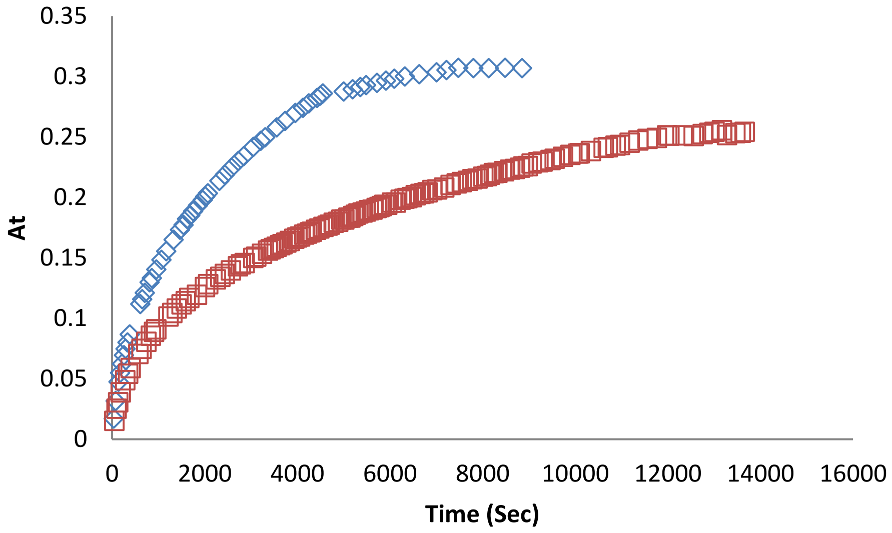
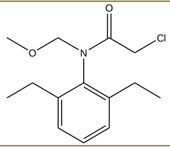
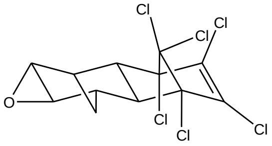


Figure 4.31: Enrichment curves of dieldrin (100 mgL^{-1}) singly (◊) and in a mixture with alachlor (O) into a 44.22 µm passive sampling membrane. Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

With dieldrin a more noticeable decrease in absorbance value was seen, from 0.3069 to 0.2542, where the increase in T_{90} being from 4246 sec to 9063 sec. These values for dieldrin are comparable to results obtained previously for the atrazine-dieldrin multi-component system (Figure 4.31).

Table 4.12: 100 mgL^{-1} alachlor-dieldrin (single and multi component) diffusing into a 44.22 µm plasticised PVC film. Diffusion coefficients and absorbance at T100 also given

		Diffusion Coefficient (cm^{2}sec^{-1})		Absorbance at T100	
Analyte	Structure	Single Component	Multi Component	Single Component	Multi Component
Alachlor		1.895 x 10^{-9}	1.152 x 10^{-9}	0.0860	0.0852
Dieldrin		5.898 x 10^{-9}	3.125 x 10^{-9}	0.3069	0.2542

As with the previous multi component system a decrease in the diffusion coefficient was seen for both compounds. This shows the effect of the competitive interaction between the two penetrants.

4.3.7.3 ALDRIN AND DIELDRIN

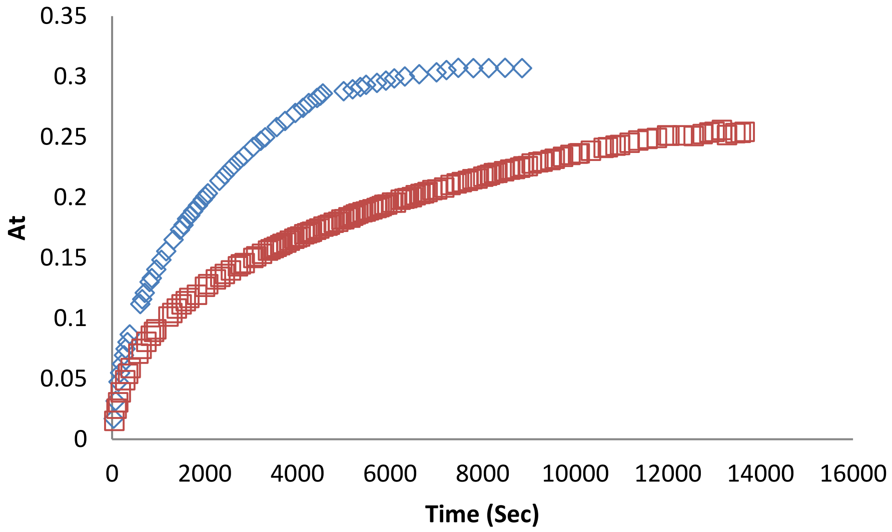


Figure 4.32: Enrichment curves of dieldrin (100 mgL^{-1}) singly (◊) and in a mixture with aldrin (O) into a 44.22 µm passive sampling membrane. Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

With the addition of a second penetrant into the system, dieldrin again showed a decrease in max absorbance values, and an increase in time taken to reach T_{90} (4246 to 9063 sec) (Figure 4.32).

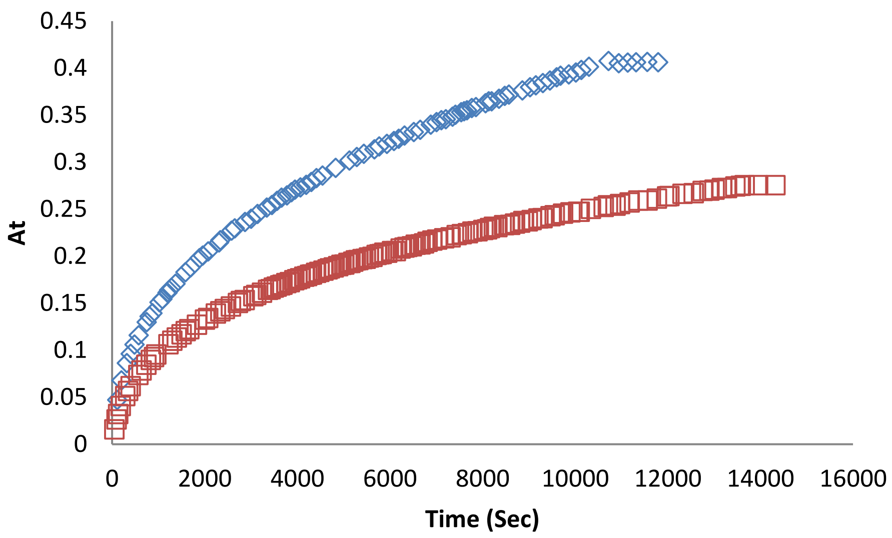
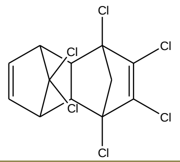
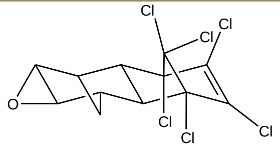


Figure 4.33: Enrichment curves of aldrin (100 mgL^{-1}) singly (◊) and in a mixture with dieldrin (O) into a 44.22 µm passive sampling membrane. Samples were taken using a PerkinElmer Spectrum GX FTIR system, resolution 4 cm^{-1}, interval 1 cm^{-1}, number of scans 4.

Aldrin followed the same trend as other pollutants once it was analysed as part of a multi component system. The time taken to reach T_{90} increased from 8131 sec to 10101 sec as expected and simultaneously a decrease in absorbance was also noted (Figure 4.33).

Table 4.13: 100 mgL^{-1} atrazine-dieldrin (single and multi component) diffusing into a 44.22 µm plasticised PVC film. Diffusion coefficients and absorbance at T_{100} also given

		Diffusion Coefficient (cm^{2}sec^{-1})		Absorbance at T_{100}	
Analyte	Structure	Single Component	Multi Component	Single Component	Multi Component
Aldrin		3.125 x 10^{-9}	2.529 x 10^{-9}	0.4066	0.2756
Dieldrin		5.898 x 10^{-9}	2.934 x 10^{-9}	0.3069	0.2543

4.4 CONCLUSIONS

ATR-FTIR was successfully used to assess the enrichment characterisation of priority pollutant analytes into polymeric membranes. ATR spectroscopy has shown itself to be a versatile tool for the investigation of the diffusion of pollutants into polymer membranes. One of the main objectives of this chapter was to present a mathematical model which was based on Fickian diffusion, which enabled the simulation of pollutant measurements and also the calculation of the diffusion coefficients for the pollutants into the novel polymeric material. The program for the simulation of the absorbance plats as a function of time was written in Matlab.

It can be observed that the quality of the fit for the diffusion data of the pollutants into PVC varies with the pollutant. The output for the ATR diffusion experiment was found to be a convolution of the evanescent wave and the liquid diffusion profile resulting in a distinguishing S shape of the data at low intensity and shorter times. The bottom of this ‘S’ shape is caused by the time the analyte takes to reach the evanescent region of the ATR crystal. Due to the thinness of the polymeric film (44 µm) this was reached rapidly. Looking at the comparison between the experimental data obtained and the simulated data one can see that the curve fit is quite similar, which indicated that the diffusion of these priority pollutants is mostly governed by Fickian diffusion.

Initial work carried out was based on the diffusion of a single analyte. This system is less complex than the multi-component system. Within the multi component system there is the effect of both components diffusing into the polymer layer, but also the competitive interaction of both compounds. For this reason a decrease in the diffusion coefficient can be seen. It had previously been reported in the literature that within multi component systems that the faster diffusing penetrant will maintain a diffusion coefficient virtually the same as within a single component system (11). In each of the three multi component systems studied dieldrin had the higher diffusion coefficient, and in each case the value was reduced with the introduction of a second penetrant. When looking at the values obtained for the diffusion coefficient of dieldrin in a multicomponent system an average of 3.04×10^{-9}

± 2.58%. From this is can be deduced that irregardless of the competing penetrant the value obtained would fall within a set range. The compounds tested against dieldrin varied in both molecular weight and polarity.

The results presented in this chapter demonstrate the value of ATR as a technique to rapidly and accurately measure diffusion in to a polymer. An IR spectrum provides direct information about the polymer and because of this insight into the potential pollutant-polymer interactions can be obtained.

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CHAPTER 5: DEPLOYMENT AND TESTING OF NOVEL AND OFF THE SHELF PASSIVE SAMPLERS

5.1 INTRODUCTION

5.1.1 DEPLOYMENT OF ENVIRONMENTAL SENSORS

The average time span for the field deployment of passive samplers is 28-30 days, however the time span of the deployment is not important once the time that the sampling devices are deployed is known. There have been published studies with deployments ranging from one week (1) to several months (2). When shorter deployments are preformed less water is being sampled and this is turn will limit some of the advantages of using a passive sampler. For longer deployments the sampling kinetics may be subject to change, from an integrative sampler to an equilibrium sampler, for selected pollutants. Other issues that can arise from longer deployments are the substantial build up of bio-film which would inhibit the passive samplers ability to accumulate chemicals (3). The longer the deployment the greater risk there is to damage or loss of the sampler, due to either water body events or vandalism.

5.1.1.1 SITE SELECTION

The selection of the site is a very important factor in the deployment plan for passive samplers. The choice of site should be made based on the goals of the study in question. Due to the accessibility of the site and logistics of the sampler deployment some flexibility in the site selection may be necessary. Some of the critical factors for the deployment of passive samplers are outlined below.

5.1.1.1.1 AVAILABLE WATER

This is the most important factor to take into consideration when selecting a deployment site for passive samplers. It is crucial that the passive sampling devices remain submerged under water thoughout the deployment period (4). If the samplers were to come in contact with air it is possible that they could be contaminated by airborne chemicals (5), and that there could be a loss of the sampled chemicals to the surrounding air environment. One other major issue with this is that one does not know how long the passive sampler was deployed under water so the estimation of average water concentration may be impossible. For this reason in many cases small streams would not have the adequate depth required to ensure that the deployment cages containing the passive samplers are completely immersed.

If in the case where sufficient water depth is not available and the site must be sampled the options are limited. Finding a deep hole or creating a hole dug into the streambed can be considered as an option. However this in turn can be problematic where there are high levels of suspended solids as it is possible that the deployment cage will become buried. Another option would be to create a temporary dam, but this option too is not favourable as it could create unpredicted consequences up and downstream due to the restricted water flow.

5.1.1.1.2 PHYSICAL ORIENTATION

The physical orientation of the deployment cage in the water body generally is not an issue once the deployment canister has openings to allow for water exchange. Orientation of the sampler cage will become an issue in deployment sites where there are high levels of suspended solids present. In these situations it would desirable to orientate the deployment cages so the area of the canister with the fewest/smallest openings is facing upstream to aid in minimizing the amount of suspended solids that may enter and remain trapped within the deployment cage.

If through study of the deployment site suspended solids are predicted to cause a problem for the deployed passive samplers, it is possible to place the deployment cage behind some sort of obstacle which will help to shield the samplers from the majority of the solids (5). One issue is that this orientation will reduce the amount of water flow to the sampling cage however the samplers may perform better as there is minimal chacge of damage to or clogging of the sampler from suspended solids.

5.1.1.1.3 VANDALISM

One of the greatest risks in the use of passive samplers in the field is vandalism (5) (6). Theft of samplers is costly not only in terms of the loss of hardware, but also in loss of data. Fieldwork studies are often planned during certain periods of time relating to the season, or land use activities and as such the timing of sampling can be important.

It is important to use careful consideration when selecting a field site. One way that can help deter vandalism is performing deployments during off-season, for fishing boats etc., periods of cooler weather and fewer daylight hours can also discourage outdoor activities. However the best option when deploying passive sampling devices is to hide and protect the samplers as much as possible and to ensure that the samplers are securely tethered (4) .

5.1.2 QUALITY CONTROL USING PASSIVE SAMPLERS

The is a large number of potential QC sample types that can be used for passive samplers (2), and as such it is common for the number of QC samples to take between 10 to 50% of the total number of samples used within the sampling study. While it is not always economically feasible to analyse a large QC set with a field deployment it is important to use some QC samples to avoid the potential compromising the results. The main QC samples can fall into two categories; blanks and spikes and are detailed in the following sections (5).

5.1.2.1 BLANKS

The main types of blanks used with passive samplers can include fabrication, field, trip and laboratory blanks (7). Fabrication blanks can often be referred to as Day 0 blanks. These blanks are fabricated at the same time as the field deployed samplers and stored under inert atmosphere until they are processed alongside the field samplers. These samplers are used to account for interferences or contamination that can occur with POCIS and Chemcatcher components during storage, processing and analysis.

Field blanks are passive samplers that are stored in airtight containers and transported to the field sites in insulated containers (8). During the deployment and retrieval of samplers, the field blanks are exposed to the surrounding air. These blanks are used to account for any contamination that can occur to the samplers during the transport to and from the study sites, and exposure to airborne contaminants during the samplers' lifetime.

Another form of QC blanks that can be used is trip blanks. These are similar to field blanks with one significant difference. These blanks are not exposed to the environment, and remain sealed during the transport to and from the deployment site. Through the use of trip blanks it is possible to account for the contamination during the transport (9). While these blanks can be used for aquatic samplers they are most commonly used for air sampling studies (5).

5.1.2.2 SPIKES

Spikes are used as a QC element to determine the recovery of the targeted chemicals and potential interferences which can be found to affect the analysis of samples (10). Spikes generally fall into two categories; matrix and procedural (5).

Matrix spikes are when the passive sampling devices are prepared using a known quantity of targeted chemicals. During this type of spiking procedure, the spike is carried out through the whole process to determine the percentage recovery of the target analytes during analysis. If multiple chemical classes are to be targeted in the environment it is common to prepare separate matrix spikes for each chemical class or analytical method.

The other spiking method that is commonly used is procedural spikes. This type of spiking method is used to determine the recovery of target analytes for a specific step within the procedure. The target analytes are prepared in a suitable solvent, without the passive sampler matrix. In some cases radio labelled or deuterated compounds can often be used to provide a rapid indication of the performance or an individual step.

5.1.3 AIMS AND OBJECTIVES

The aim of this chapter is to review the results obtained after environmental exposure of the developed passive samplers. Two sites were selected for this study, Ringsend, Co. Dublin and Lough Hyne, Co. Cork. Four plasticised samplers;

diisononyl adipate (DA), methyl laurate (ML), butyl octyl phthalate (BOP), and dimethyl phthalate (DMP), and one unplasticised sampler were deployed for one month periods. These samplers were then extracted, as detailed in Chapter 3 (Section 3.3.3) and analysed using the GC-MS method previously outlined in Chapter 2 (Section 2.3). For one month a series of commercial samplers; pesticide-POCIS, pharmaceutical-POCIS and Chemcatcher were deployed in Ringsend alongside the novel plasticised samplers developed in Chapter 3 for comparison purposes.

5.2 MATERIAL AND METHODS

All plasticisers were purchased from Scientific Polymer Products, Ontario. All other chemicals and solvents were purchased from Sigma-Aldrich, Tallaght, Ireland and used without further purification. SPE cartridges used were Isolute C18, 6 mL.

5.2.1 SODIUM SULPHATE CARTRIDGES

Using a blunt metal stick the frits and the sorbent of a SPE cartridge were removed to obtain an empty 6 mL SPE cartridge. These cartridges and frits were then rinsed in IPA to remove all traces of the sorbent that remained. After they had been rinsed they were sonicated in methanol to ensure cleanliness and to avoid any cross contamination from the previous sorbent.

The lower frit was returned to the cartridge and to ensure complete dryness, the cartridge and lower frit were dried over vacuum for a period of 15 min. 500 ± 0.02% mg of sodium sulphate (granular) (n=7) was weighed out and deposited into the SPE cartridge. The upper frit was then attached slowly to ensure that any sorbent attached to the side of the cartridge is removed and pressed down to the main body of sorbent.

5.2.2 EXTRACTION OF PASSIVE SAMPLING DEVICES

5.2.2.1 CHEMCATCHER NON POLAR

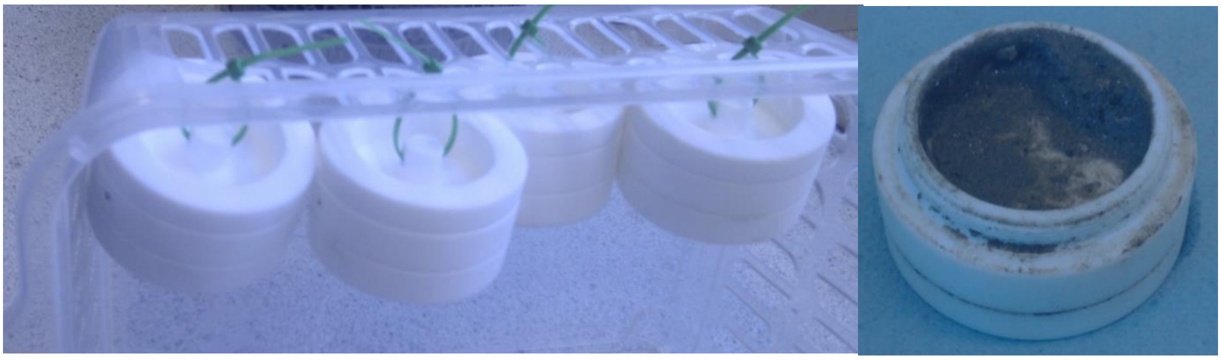


Figure 5.1: Non-polar Chemcatcher samplers before (left) and after (right) 32 day exposure in Ringsend (October-November 2011)

After the Chemcatchers were retrieved from the deployment site and brought back to the laboratory they were carefully rinsed with MQ grade DI water. The Chemcatcher was separated out into three distinct pieces, and the diffusion limiting LDPE membrane was carefully removed from the top of the C18 Empore disk using tweezers. The membrane was then rinsed with 5 mL of acetone in order to remove any remaining n-octanol.

The C18 Empore disk was placed into a 25 mL disposable extraction vial and the acetone wash from the membrane was carefully transferred into the same. The vial containing the C18 Empore Disk and 5 ml of acetone was soaked in an ultrasonic bath for a period of 5 min (1). The vial was then removed from the ultrasonic bath and the exterior was dried in order to prevent the occurrence of any contamination. This extract was then transferred to a prepared drying cartridge.

5 mL of 50:50 (v/v) 2,2,4 trimethylpentane:ethyl acetate was added to the vial containing the Empore disk and soaked in the ultrasonic bath for five min. This extract was then filtered using sodium sulphate drying cartridge prepared previously, (Section 5.2.1) into the same glass receiving vial. The vial containing the disk was then rinsed with 2 mL of the 50:50 (v/v) mixture of 2,2,4 trimethylpentane:ethyl acetate, and this aliquot was also filtered using the same sodium sulphate cartridge.

The extract was then reduced to approximately 0.45 ml (when only n-octanol remained) under a gentle flow of nitrogen. The internal standard, 50 µL of 10 ng μL^{-1} of D10 anthracene in n-octanol, was added and the extract was then carefully transferred to a 2 mL GC vial where the total final volume was adjusted to 500 µL through the addition of n-octanol.

5.2.2.2 POCIS

Figure 5.2: POCIS samplers before (left) and after (right) 32 day exposure in Ringsend (October-November 2011)

As it has been reported previously that the solid sorbent inside the POCIS is generally the only section extracted and that the membranes are discarded this method was utilised (Section 1.4.4.2) (5). Studies have determined that POCIS membranes contain only a small part of the sampled chemicals, but that in a 21 day or longer study this amount is minimal in comparison to the concentration of the target analyte contained in the sorbent. Published sampling rates for the POCIS do not consider the membrane, and therefore any TWA concentrations calculated from both sorbent and membrane would be an over estimation of the actual concentration.

A frit was placed in the bottom of an empty SPE cartridge, and the cartridge and the frit were then rinsed with the solvents, to be used during the extraction process and dried. With the pharmaceutical POCIS configuration 40 mL of methanol was used to extract the pollutants from the sorbent. With the pesticide-POCIS, 50 mL of 1:1:8 (v:v:v) mixture of methanol:toluene:dichloromethane was used (5).

The POCIS sampler was carefully opened over a funnel and was rinsed into the SPE cartridge using water. Once the sorbent has been fully removed from the POCIS sampler a second frit is placed onto of the sorbent to prevent mixing as the extraction solvent is added.

1 mL of these extracts where taken and analysed using the GC (Section 2.3.4) however the signal to noise ratio was very low. It was decided to take the remaining 39 mL of extract, evaporate it down under nitrogen and reconstitute to 1 mL using the extraction solvents mentioned above.

5.2.2.3 NOVEL PASSIVE SAMPLERS

Novel passive samplers were prepared as outlined in Chapter 3.

5.2.3 WATER ANALYSIS

SPE Analysis was carried out as outline in Chapter 2, Section 2.2.

5.3 RESULTS AND DISCUSSION

5.3.1 SELECTION OF PASSIVE SAMPLING DEVICES

A brief screening study of four novel PSDs was carried out against seven different pesticides; isodrin, aldrin, endrin, dieldrin, alachlor, atrazine and mecoprop. All of these pesticides have been shown previously (Table 1.2) in relation to their structures and chemical and physical properties with the exception of mecoprop. Mecoprop whilst not mentioned in Annex X of the WFD but is a common use herbicide and was added to the monitoring programme by the Irish EPA (11).

5.3.1.1 POCIS

There are two configurations of POCIS that are commercially available and both were selected for use in this field trial. While the two configurations are referred to pesticide-POCIS and pharmaceutical-POCIS, it should be noted that each type will sample a wider range than just these two groupings (193) (12). The difference between these two configurations is the sorbent. The pesticide-POCIS uses a triad or sorbents, Isolute® ENV+ and Ambersorb® 1500 dispersed on S-X3 BioBeads® (13). This was the original configuration and was tested for pesticides and hormones. As further work was carried out and additional compounds added to the list of target pollutants it was found that groups of pharmaceuticals with multiple functional groups were difficult to recover from the selected sorbent.

Once this had been observed in the studies a second POCIS, the pharmaceutical-POCIS, was developed using Oasis HLB (14). Oasis HLB is usually considered a universal sorbent for environmental analysis and has been seen to extract a wide assortment of chemical classes from water bodies. One benefit of using such a universal sorbent is the wide range of published solvent combinations that have been used for extraction previously.

5.3.1.2. CHEMCATCHER

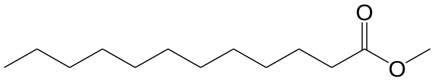
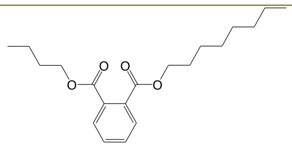
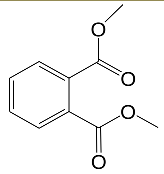
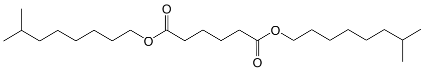
Chemcatcher is a passive sampling device that can be used to calculated TWA concentrations of pollutants in water (15). The sampler consists of a water tight PTFE body, with a 3M EmporeTM receiving phase disk, covered with a thin diffusion limiting membrane (16). The sampler has been previously deployed in the field for extended time periods ranging from days to weeks.

After the Chemcatcher is retrieved from the environment the pollutants are eluted from the Empore disk and are analysed within the laboratory. When calculating TWA concentrations, the samplers must be calibrated in order to determine an uptake rate for the target pollutants. Sampling rates for many pollutants of interest have previously been published.

5.3.1.3 NOVEL PASSIVE SAMPLING DEVICES

When deciding how to deploy the novel passive samplers developed in Chapter 3, it was determined to put out a series of samplers utilising different compositions. The plasticisers looked at are included in the table below.

Table 5.1: Overview of plasticisers used in the four deployed configurations of novel passive samplers deployed in both Ringsend and Loch Hyne over the course of the deployment period (2011)

Plasticiser	Structure	Mol. Formula	Log K_{ow}
Methyl Laurate (ML)		$C_{13}H_{26}O_2$	5.49
Butyl Octyl Phthalate (BOP)		$C_{20}H_{30}O_4$	6.95
Dimethyl Phthalate (DMP)		$C_{10}H_{10}O_4$	1.64
Diisononyl adiapte (DA)		$C_{24}H_{46}O_4$	9.24

Methyl Laurate had previously been looked at during the development of the passive sampling device. Both DMP and BOP have previously been studied for their anti fouling properties (17). It was found from previous studies that increasingly branched and longer chain phthalic esters showed better anti-fouling properties than shorter chain phthalic esters. This property alongside the affinity for the target analytes will aid in the deployment of the samplers, the greater anti-fouling properties that the membranes show, the less of a biofilm that is formed on the surface. This biofilm will alter the sampling rate of the pollutants, and in doing so will offset the prediction of TWA concentrations as the sampling rate will not remain uniform.

Table 5.2: Results showing percentage recoveries for 7 pesticides after exposure to four distinct plastised membranes after a period of 24 h. Mobile phase 70:30 ACN:DI H_2O, wavelength 210 nm, flow rate 1.0 mlmin^{-1}

Log K_{ow}	Compound	Methyl Laurate mgL^{-1}	DMP mgL^{-1}	BOP mgL^{-1}	PVC mgL^{-1}
2.84	Mecoprop	**36.5**	24.0	34.0	20.7
3.05	Atrazine	**131.4**	39.6	100.4	17.3
3.05	Alachlor	**208.3**	99.98	160.1	35.3
4.48	Dieldrin	30.9	18.1	**84.1**	51.5
4.88	Endrin	92.2	86.8	**141.0**	130.6
6.23	Aldrin	64.8	58.13	**83.2**	53.8
6.23	Isodrin	48.0	39.67	**74.6**	68.6

As can be seen from the above results an affinity of plasticiser to Log K_{ow} of the target compounds can be seen (Table 5.2). For the more polar compounds; mecoprop, atrazine and alachlor, an affinity toward Methyl Laurate wasobserved. Whereas when looking at the more non polar compounds; dieldrin, endrin, aldrin and isodrin an affinity for the longer chained plasticiser, BOP, can be seen. Alongside the plasticised passive sampling devices an unplasticised passive sampler was also deployed for comparison purposes.

5.3.2 SAMPLING SITES

Two sampling sites were selected and a described in detail below.

5.3.2.1 RINGSEND

Ringsend is an inner suburb of Dublin, and is located on the south bank of the River Liffey approximately 2 km east of the city centre. This site was selected in conjunction with Dr. Brian Quinn, NUI Galway, and his student Ms. Gillian McEniff, DCU. The site is positioned 200 m from the outflow pipe of Ringsend Waste Water Treatment plant.

The Ringsend Waste Water Treatment Plant (WWTP) is located on the Poolbeg peninsula close to the power stations and the area of Dublin Port. Ringsend WWTP was licensed by the EPA (Register number D0034-01) on the 27th July 2010 to discharge treated wastewater effluent to the Lower Liffey Estuary and serves the greater Dublin agglomeration. This agglomeration is the largest in Ireland with a measured population equivalent of 2.45 million (maximum weekly average) in 2010. The influent that is treated in Ringsend WWTP is composed of domestic wastewater, commercial wastewater, licensed trade effluents, surface water from combined sewers, surface water infiltration, groundwater infiltration, saline infiltration and tinkered wastewaters (18).

Prior to 2003, Dublin City Sewage only received primary treatment at Ringsend. Under the Urban Wastewater Directive, secondary treatment became mandatory and the dumping of sludge at sea had to cease by the end of 1998. While designing the upgrade of this plant, following good engineering practice, the plant was designed in regard to projections of population growth and industrial development up to the year 2020. To date, projections in population growth have been in target when compared to the Census values of 2002 and 2006 (19).

5.3.2.1.1 APRIL –MAY 2011

A series of five novel passive sampling devices were deployed 200 m from the outflow pipe of Ringsend WWTP for a series of one month periods. After the samplers had been retrieved they were extracted as outlined in Chapter 3 previously (Section 3.3.2.2). These extracts were then analysed using GC-MS, and identification of peaks was carried out based on the matching of MS spectra to the NIST98 database.

After analysis of the five types of novel samplers it was found that no priority pollutants mentioned in Annex X of the WFD were found to be present in the extracts. The most commonly detected chemicals were several plasticisers, including methyl laurate which was used in one of the plasticised devices, and a series of long chain alkanes both branched and unbranched. In the BOP doped passive sampling devices 2-Anthracenamine (CAS: 613-13-8) was identified and if released to water, 2-anthracenamine may adsorb strongly to suspended solids and sediments, bio accumulate significantly in aquatic organisms, or photolyze in near-surface waters (estimated midday, midsummer half-life less than 4.5 days).

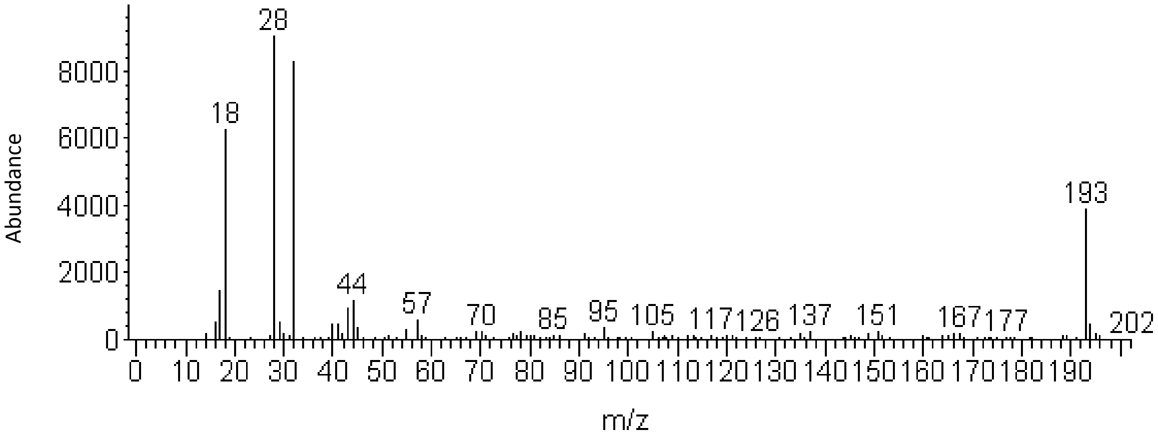


Figure 5.3: Mass spectra of 2-anthracenamine (CAS: 613-13-8) detected in the extract of the BOP doped passive sampler after analysis with GC-MS. (Initial temperature 40°C

(hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min))

When extracting the DA doped samplers, one of the compounds that was identified was Methylsulfonylmethane (CAS: 67-71-0) (Figure 5.4).

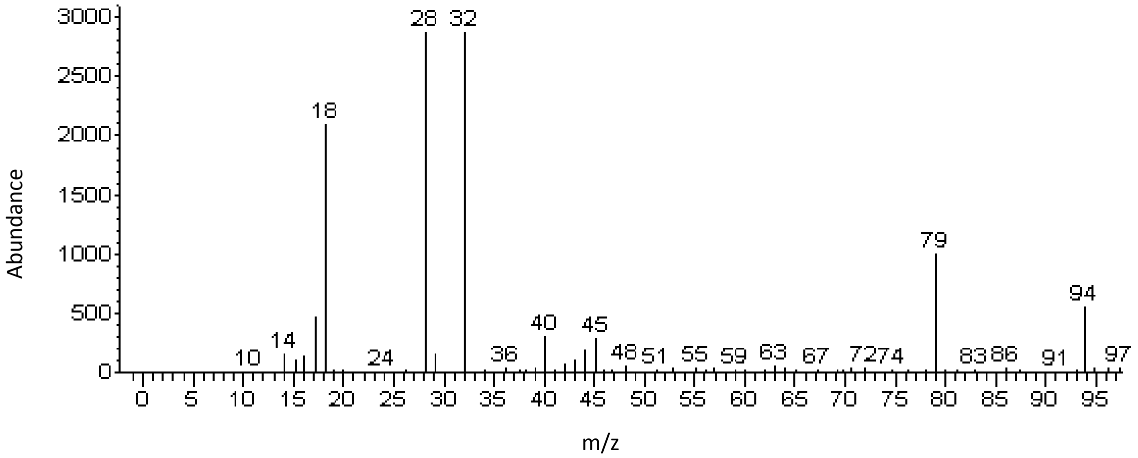


Figure 5.4: Mass spectra of Methylsulfonylmethane (CAS: 67-71-0), also known as dimethyl sulfone detected in the DA doped samplers after exposure to seawater beside the Ringsend outflow pipe for a month period between April-May 2011. Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min).

Methylsulfonylmethyl (MSM) is an organosulfar compound that is considered relatively chemically inert. Occurrence of methylsulfonylmethane can be attributed to some primitive plants and it is also found present in low concentrations in many foods and beverages and is marketed as a dietary supplement. Phthalide (CAS Number: 87-41-2) was detected in the extract from the DMP passive sampling devices (Figure 5.5). Phthalide is an organic compound that can serve as the core chemical structure for a series of dyes (phenolphthalein), fungicides (tetrachlorophthalide) and natural oils (butylphthalide).

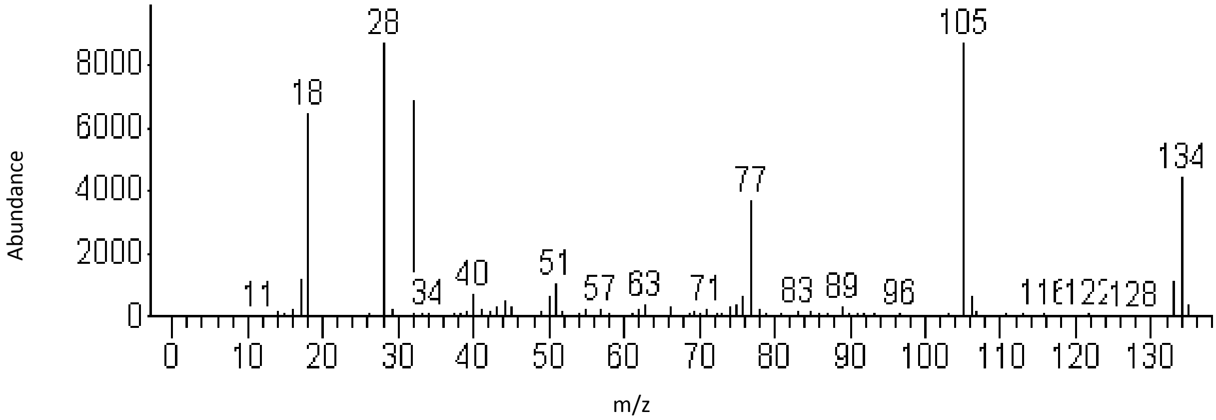


Figure 5.5: Mass spectra of Phthalide (CAS: 87-41-2), also known as 1 (3 H) Isobenzofuranone detected in the DMP doped samplers after exposure to seawater beside the Ringsend outflow pipe for a month period between April-May 2011. Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min)

Butylated hydroxytoluene (BHT) (CAS: 128-37-0) was detected in both the BOP and DA passive samplers as can be seen from the spectra below (Figure 5.6).

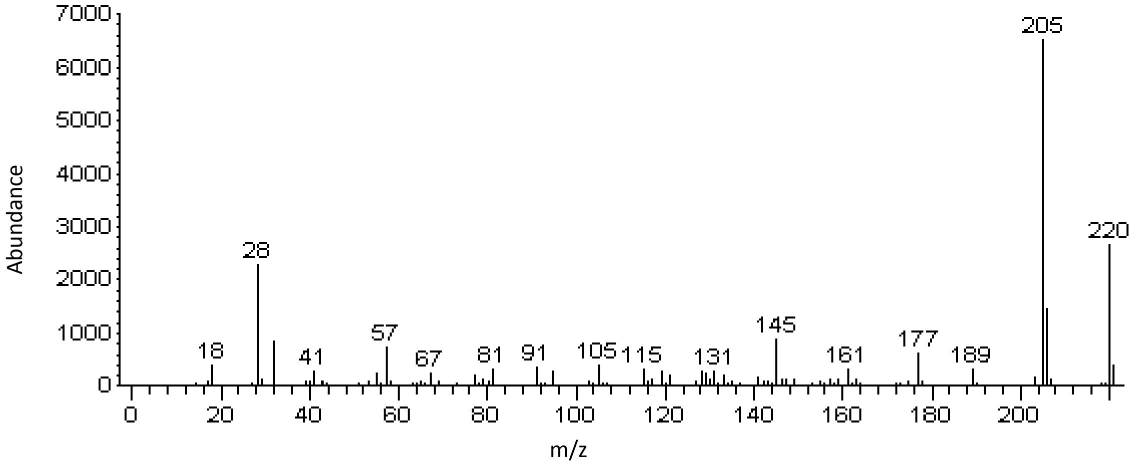


Figure 5. 6: Mass spectra of Butylated hydroxytoluene (CAS: 128-37-0) was detected in both the BOP and DA doped samplers after exposure to seawater beside the Ringsend outflow pipe for a month period between April-May 2011. Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min).

BHT has found application in the food and cosmetic industry as a chemical antioxidant similar to butylated hydroxyanisole (20).

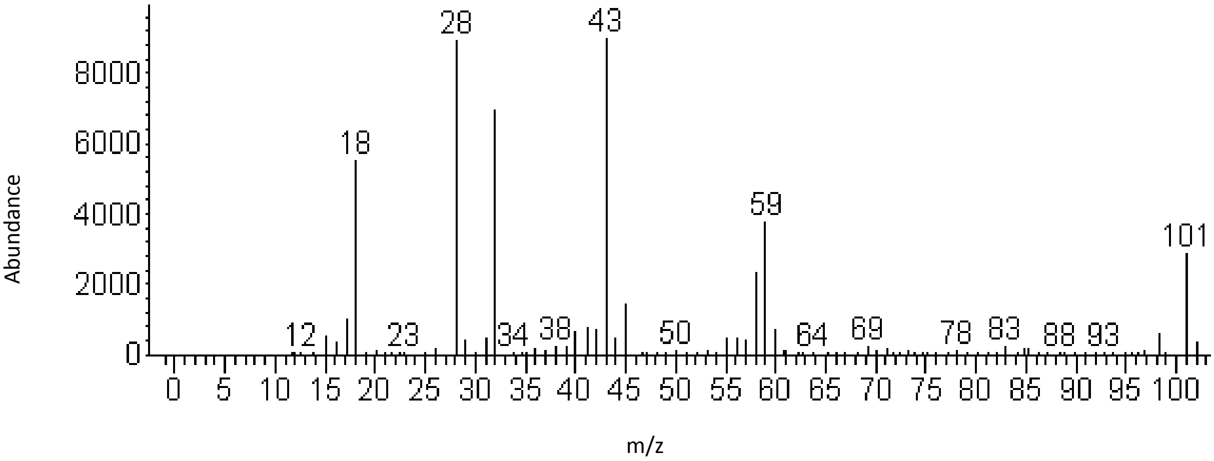


Figure 5.7: 4 Hydroxy, 4-methyl 2-pentanone (CAS: 123-42-2) more commonly known as diaceone alcohol was detected in DA doped passive samplers after a one month exposure in Ringsend.

4-Hydroxy, 4-methyl, 2-pentanone (CAS: 123-42-2) was detected in extracts from DA passive samplers (Figure 5.7). This compound is more commonly known as diacetone alcohol and is a chemical compound that is used as a common synthetic intermediate, that has also found use in cellulose ester lacquers, wood stains and permanent markers (21) and can be used as a solvent for water based coatings. Diacetone alcohol has found use as a solvent extractant for processes involved in the purification of resins and waxes (22).

While pollutants were detected using these novel passive sampling devices, the target pollutants, both the pesticides and the PAHs mentioned within the WFD were not detected at this sampling site during the deployment time.

5.3.2.1.2 AUGUST-SEPTEMBER 2011

As with the previous deployment five novel passive sampling devices were deployed, four plasticised configurations (Table 5.1) and an unplasticised sampler. A water sample was also taken on the day that the samples were retrieved for comparison to values found in the extracts from the passive samplers and the results can be seen outlined below (Table 5.3).

Table 5.3: Results obtained from seawater sample taken at Ringsend on 3/8/11. Sample clean up was carried out using SPE method described previously.

R. Time	Library/ID	CAS
8.2817	2 Ethylhexanol	104-76-7
9.0266	1-Octanol	111-87-5
10.4937	Cyclopentasiloxane, decamethyl-	541-02-6
10.7254	Octanoic Acid	124-07-2
12.8011	Hexadecane	544-76-3
14.2864	Tetradecane	629-59-4
15.5627	4 Phenyltoluene	644-08-6
15.8761	2,4 Di-T-butylphenol	96-76-4
15.9306	Butylated Hydroxytoluene	128-37-0
16.9299	3-Eicosene, (E)-	74685-33-9
21.6855	Dibutyl phthalate	84-74-2
22.3759	Diamthazole	95-27-2
23.6795	Butyl isobutyl phthalate	17851-53-5

It can be seen from the above results that even with a pre-concentration factor of 500 that no priority pollutants were detected in the seawater. These samples were analysed using GC-MS, and peaks were identified using the NIST98 MS spectra database. Compounds that were detected include a plasticiser, butyl isobutyl phthalate (CAS: 17851-53-5) and a pair of higher alkanes, hexadecane (CAS: 544-76-3) and tetradecane (CAS: 629-59-4).

As with the previous deployment in Ringsend no priority pollutants were detected. A series of plasticisers including diisooctyl phthalate, dibutyl phthalate, methyl laurate, dimethyl phthalate, butyl isobutyl phthalate were detected in the samplers. Methyl laurate and dimethyl phthalate that was detected can be attributed to two of the novel samplers that were deployed in the field.

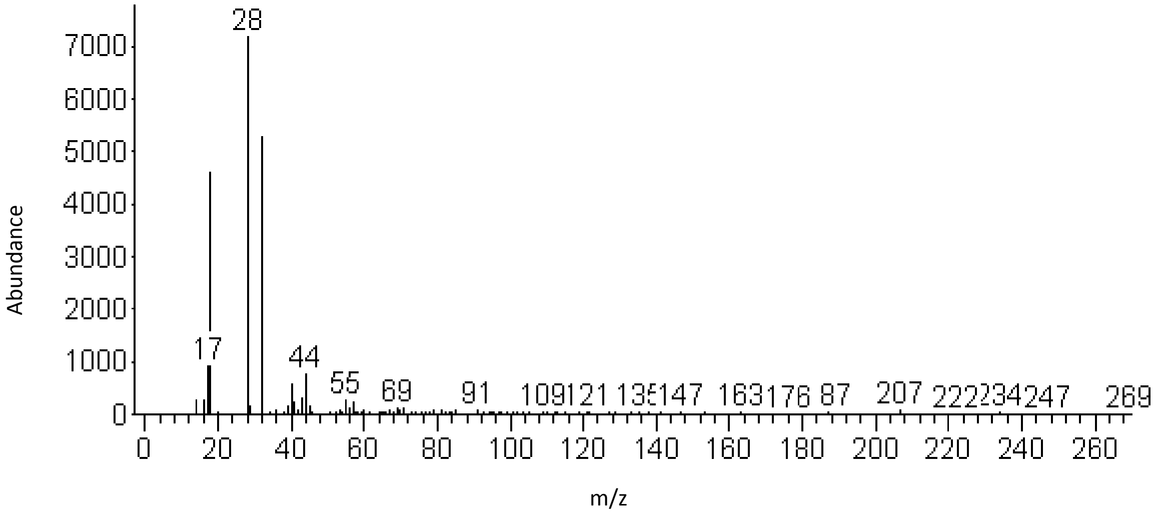


Figure 5.8: Mass spectra of Desmethyldoxepin (CAS: 1225-56-5), a metabolite of the antidepressant Doxepin (CAS: 1668-19-5) were detected in three of the five samplers deployed in Ringsend in the period of August to September 2011. Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min)

Desmethyldoxepin (CAS: 1225-56-5) was detected in three out of the five samplers (Figure 5.6), with the exception of the unplasticised and the ML doped samplers. Desmethyldoxepin is a metabolite of Doxepin (CAS: 1668-19-5) which is a psychotropic agent that has tricyclic antidepressant and anxiolytic properties (23). This drug has been marketed under several names; Doxal (Orion) Deptran, SInquan and Sinequan (Pfizer).

As with previous deployments in Ringsend a series of higher alkanes were detected in the extracts from the passive samplers. Higher alkanes can be defined as alkanes having nine or more carbon atoms. Alkanes from nonane (C9) to hexadecane (C16) are liquids with higher viscosity and as the chain length increases become less suitable for use in gasoline. Instead these compounds are found as a major substituent of diesel and aviation fuel. As the deployment site is within city limits, and with the high population equivalent that is allocated to the WWTP there is the potential for large quantities of these chemicals.

During this time period no priority pollutants were detected either from the sampler extracts or from the water sample obtained from the deployment site.

5.3.2.2 LOUGH HYNE

Lough Hyne has been the subject of many marine environmental studies even as far back as the 19th century. Lough Hyne is a marine lake in West Cork, Ireland approximately 5 km southwest of Skibbereen. Lough Hyne is relatively small, 0.8 x 0.6 km. The lough exhibits general salinities of 34.6-34.8 and is regarded as fully marine.

Lough Hyne is a deep landlocked bay that is joined by a narrow channel (Barloge Creek) to the sea. It is situated on alternating bands of lower Old Red Sandstone and Carboniferous slates. Approximately 4,000 years ago, in post glacial times it was a fresh water lake, however due to the post glacial rise in the sea level it is now saline. Due to the narrowness of the connecting sea channel, the tidal fluctuations are reduced to a value of approximately 1 m, and due to this the area of the intertidal communities is confined to a narrow band that runs along the shore line. Due to the fact that Lough Hyne is nearly land-locked and that there is relatively little tidal exchange of water, the lake is vulnerable to the effects of eutrophication.

5.3.2.2.1 DEPLOYMENT 10TH APRIL- 10TH MAY 2011

The series of five samplers were deployed in Loch Hyne in early April 2011 and left for a period of one month. After this deployment the samplers were retrieved and extracted prior to analysis on the GC-MS. After analysis of these samplers, as with the Ringsend deployment, no pollutants were detected. Unlike the results obtained from the Ringsend deployment there was significantly less detection of higher alkanes with only distinct compounds; octadecane, dodecane and tridecane being detected from the sampler extracts. This could be explained by looking at the difference in the locations of the deployment sites. The site in Ringsend is in an urban setting, whereas Lough Hyne is within a more rural setting. Other compounds that were detected were a series of plasticisers including several from the phthalate family. These can be explained due to the presence of phthalate plasticisers within the sampling devices, BOP and DMP, and several of the other phthalates detected, Butyl 2-ethylhexyl phthalate (CAS: 85-69-8), methyl ethyl phthalate (CAS: 34006-77-4), dimethyl isophthalate (CAS: 1459-93-4) and dibutyl phthalate (84-74-2) could be simply degradation products.

Upon retrieval of these sampling devices SEM images were obtained to see the effect of plasticiser type on bio-fouling of novel sampling devices. Images below are shown for diisononyl adipate doped passive samplers (Figure 5.9_ and methyl laurate samplers (Figure 5.10)

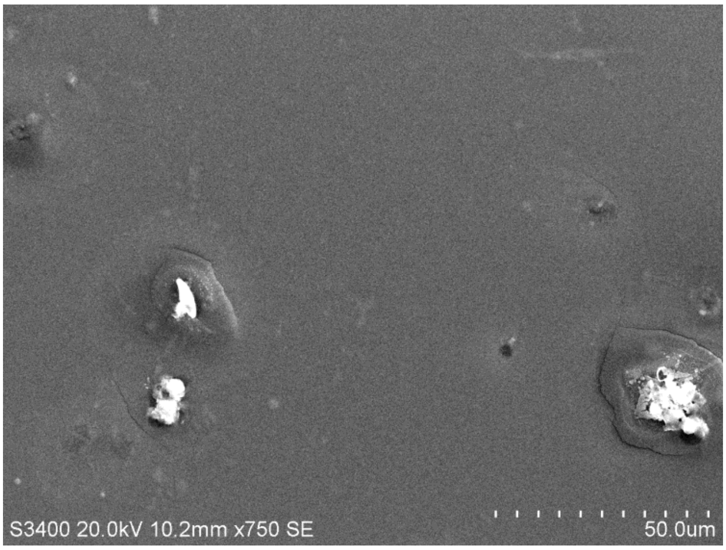


Figure 5.9: SEM images of diisononyl adipate doped passive samplers after a one month deployment in Lough Hyne. (April –May 2011) (50 µm)

The difference in fouling can be seen clearly from the two images seen here. The methyl laurate doped samplers (below) show a large degree of microbial growth in comparison to that of the diisononyl adipate doped samplers (above). This could be in part based on the difference in chain lengths of the two plasticisers shown with methyl laurate having a significantly shorter unbranched chain length (C_1) in comparison to the branched longer chain (C_9) of diisononyl adipate.

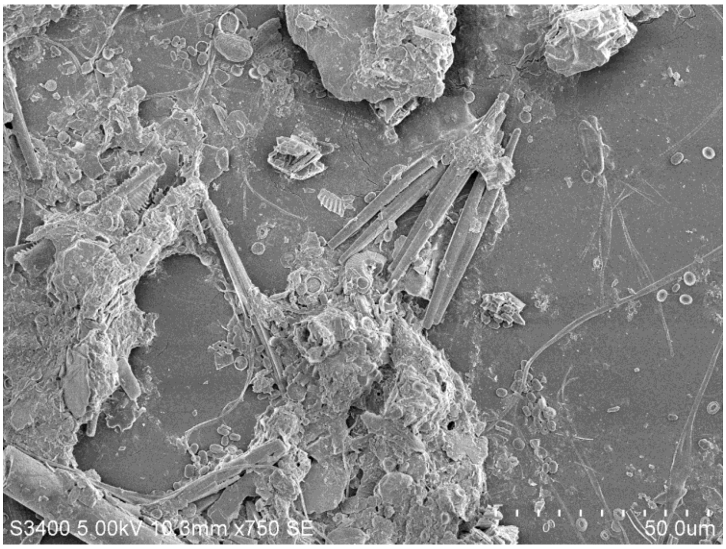


Figure 5.10: SEM Image of methyl laurate doped samplers (bottom) after a one month deployment in Lough Hyne. (April –May 2011) (50 µm)

Another reason for the difference in growth on the two samplers could be explained by plasticiser leeching. As has been mentioned previously methyl laurate was being detected in the plasticised samples post deployment when the extracts from the samplers were analysed. This could have been attributed to methyl laurate being present in the water body, but it was possible that the methyl laurate was leaching from the plasticised disk and was then diffusing into the other samplers. A week long leeching study was carried out as outlined by Chapman *et al.* (17) from which it was found that both methyl laurate and dimethyl phthalate showed a high percentage of plasticiser leaching in comparison to the longer chain plasticisers. The increase in bio-fouling that can be seen with the methyl laurate doped samplers can be attributed to the fact that after the one month deployment period there was a significant amount of plasticiser leeching. Previous work carried out within the group has shown that diisononyl adipate showed anti-fouling ability which can be seen from the imaged disk (Figure 5.9)

5.3.3 COMPARISON OF NOVEL PASSIVE SAMPLING DISKS WITH COMMERCIALLY AVAILABLE SAMPLERS

Samplers for this work were deployed during October-November 2011. On the day the passive sampling devices were removed from the water two water samples were collected. One was a sample of water at the deployment site, and the other a 24 h composite sample of effluent from the Waste Water Treatment Plant. These samples were collected to act as a comparison to the pollutants detected in the deployed passive samplers.

Table 5.4 Results obtained from seawater sample taken at Ringsend on 9/11/11. Sample clean up was carried out using SPE (Strata X 500mg Cartridge, eluted with 1 mL IPA, 1 mL of Acetonitrile, evaporated to dryness and reconstituted with 1 mL of Acetonitrile). GC-MS Method: Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min)

RT	*Library/ID*	*CAS*
15.8723	2,4-Di-T-Butylphenol	96-76-4
16.272	Acetamide, N,N'-[(3.beta.)-18-hydroxypregn-5-ene-3,20-diyl]bis-	055555-60-7
19.5333	Nordefrin	6539-57-7
21.9951	Benzeneethanamine, 4-benzyloxy-3-fluoro-.beta.-hydroxy-5-methoxy-N-methyl	1000116-29-9
22.304	5-[4-(Dimethylamino)cinnamoyl]acenaphthene	1000224-02-6
23.1715	Dihydrotazettadiol	1000111-43-5
30.2572	Benzeneethanamine, 2-fluoro-.beta.,5-dihydroxy-N-methyl-	103439-07-2

As can be seen from the above table none of the pollutants mentioned in Annex X of the WFD were found to be present in the seawater sample. Some pharmaceutals were however found but were not quantified. Nordefrin (R. Time: 19.53) can also be known as α-methylnorepinephrine, and is a sympathomimetic amine that has found use as both a tropical nasal decongestant and as a vasoconstrictor in dentistry. Nordefrin can also be found as the metabolite of methyldopa, an anti hypertensive drug (Aldomet Tablets, Aspen).

Table 5.5: Results obtained from 24 h composite effluent sample taken at Ringsend WWTP on 8-9/11/11. Sample clean up was carried out using SPE (Strata X 500mg Cartridge, eluted with 1 mL IPA, 1 mL of Acetonitrile, evaporated to dryness and reconstituted with 1 mL of Acetonitrile). GC-MS Method: Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min)

RT	Library/ID	CAS
4.4795	hexamethylcyclotrisiloxane	541-05-9
9.1443	Arsenous acid, tris(trimethylsilyl) ester	55429-29-3
9.8301	Hexanoic acid, 2-ethyl-	149-57-5
10.7749	Octanoic Acid	124-07-2
11.706	Cyclotetrasiloxane, octamethyl-	556-67-2
21.24	Caffeine	58-08-2
21.7941	4-methoxyamphetamine	23239-32-9
22.4845	Dihydrotazettadiol	1000111-43-5
22.9705	5-(4-Nexyloxybenzoyloxy)-2-(4-nitrophenyl)pyrimidine	136240-26-1
25.4187	Ethyl N'-isopropylureidoacetate	29346-49-4
25.6458	Nortriptyline	72-69-5
26.4316	Benzeneethanamine, 4-fluoro-.beta.,3-dihydroxy-N-methyl-	103439-06-1
27.0357	Fluoxetine (Prozac)	54910-89-3
27.9532	Epinephrine	51-43-4
28.7981	Metaraminol	54-49-9
30.5968	l-Guanidinosuccinimide	1000130-20-8
30.9011	2-Amino-1-(O-methoxyphenyl)propane	15402-84-3

Similar to the seawater sample obtained in November none of the priority pollutants were detected in the 24 h effluent composite sample (Table 5.5). Whilst looking at the mass spectrum results from this sample a series of pharmaceuticals were detected.

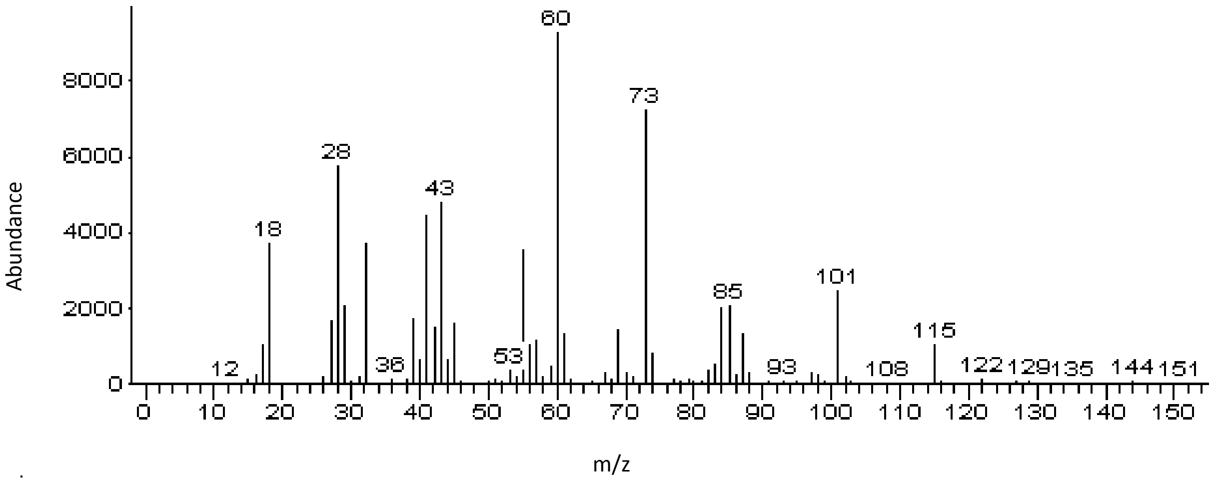


Figure 5.11: Mass spectrum identified as Octanoic Acid (CAS: 124-07-2) detected in the effluent 24 h composite sample obtained from Ringsend WWTP. GC-MS Method: Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min)

Octanoic Acid (CAS: 124-07-2) whichcan also be referred to caprylic acid was detected in the composite sample (Figure 5.11) and can be found naturally in coconut oil, palm oil, butter fat and also in human breast milk. Caffeine (CAS: 58-06-2) was also detected in the effluent composite sample (Figure 5.12), and while some of this would be related to caffeinated beverages, there are many pharmaceutical drugs that utilise caffeine as an addition active pharmaceutical ingredient (API), e.g. Anadin extra, Lemsip Cold and flu capsules, Solpadeine tablets and Tramil Analgesic capsules.

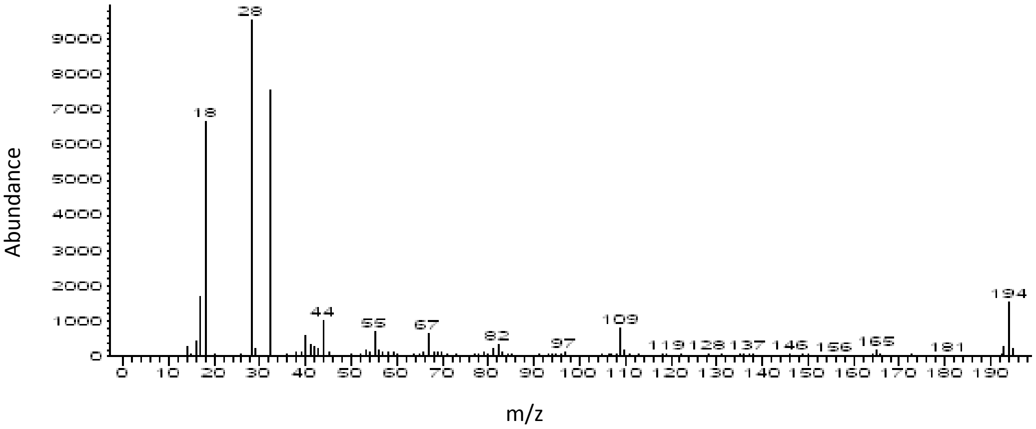


Figure 5.12: Caffeine detected in the 24 h composite effluent sample obtained from Ringsend WWTP (8/11/11). GC-MS Method: Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min)

4-methoxyamphetamine (PMA) was also detected in the sample and is a serotonergic drug of the amphetamine class. Unlike 2-MA and other drugs within in this class, PMA does not produce stimulant or euphoriant effects and behaves more like an antidepressant though it does have some psychedelic properties. PMA can occasionally be found in tablets that are labelled as MDMA (also known as ecstasy). Nortriptyline (CAS: 72-69-5) is in a class of drugs known as tricyclic antidepressants (TCA). Nortriptyline is a second generation tricyclic antidepressant (TCA) and is used for the treatment of major depression and childhood bedwetting. Fluoxetine (CAS: 54910-89-3) which is an active ingredient in Affes Capsules (Astellas Pharma Co. Ltd), Gerozac capsules (Gerard Laboratories) and more commonly known Prozac (Eli Lilly and Company (Ireland) Limited) was also detected. Another API that was detected in this sample was epinephrine (CAS: 51-43-4) which can also be known as adrenaline. This products available in Ireland from the International Medication Systems (UK) Ltd and is marketed as Epinephrine Injection 1:10000 Sterile Solution Minijet.

5.3.3.1 POCIS

Two configurations of POCIS were deployed at the Ringsend Outflow pipe from the 7th October to -the 8th November 2011 (32 day deployment). When looking at the analysed extracts of these samplers it was found that within the pesticide-POCIS no priority pollutants were detected.

In all three of the pesticide POCIS deployed levels of caffeine were found (Figure 5.13). Bartelt-Hunt *et al.* (24) reported a sampling rate for caffeine of 0.27 $Lday^{-1}$.

Using the following equation the concentration of the pollutant in water can be calculated.

$$C_w = \frac{N}{R_s t} \qquad \text{(Eq. 5.1)}$$

Where N is the amount of chemical accumulated by the sampler (ng), Rs is the sampling rate ($Lday^{-1}$) and t is the exposure time (d). As all of the above values were known the TWA of caffeine in water was able to be calculated and was determined to be 59.4 ngL^{-1} ± 5.6%.

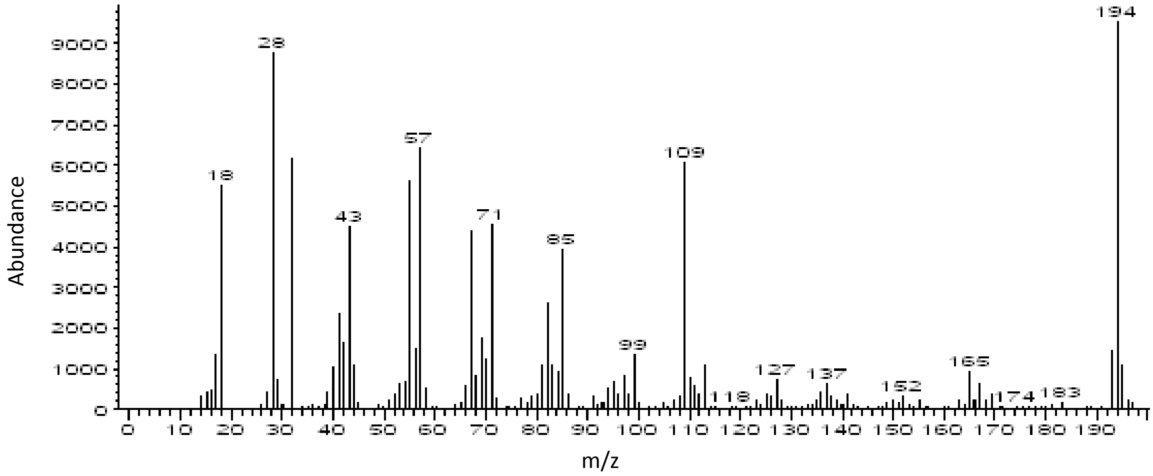


Figure 5.13: Mass spectrum of Caffeine extracted from pesticide-POCIS after a 32 day exposure in the Ringsend deployment site (October-November 2011). GC-MS Method: Initial temperature 40°C (hold 2 min), 9 $^{o}Cmin^{-1}$ to 170 °C, 3 $^{o}Cmin^{-1}$ to 205 °C, 1$^{o}Cmin^{-1}$ to 208 °C, 20 $^{o}Cmin^{-1}$ to 290 °C (hold 2 min)

Concentration levels of caffeine previously reported in water bodies has shown a large range of concentration values from 8-32 ngL^{-1} on the Mediterranean coast (25) to 16.3 – 980.1 mgL^{-1} downstream from a series of four WWTPs in Nebraska (24).

Within the pharmaceutical-POCIS a compound mentioned in Annex X of the WFD was detected. Atrazine was detected at a concentration of 3.5 ngL^{-1} which is 568 fold lower than the maximum allowed concentration in both freshwater and marine water as set by the EPA (Figure 5.14).

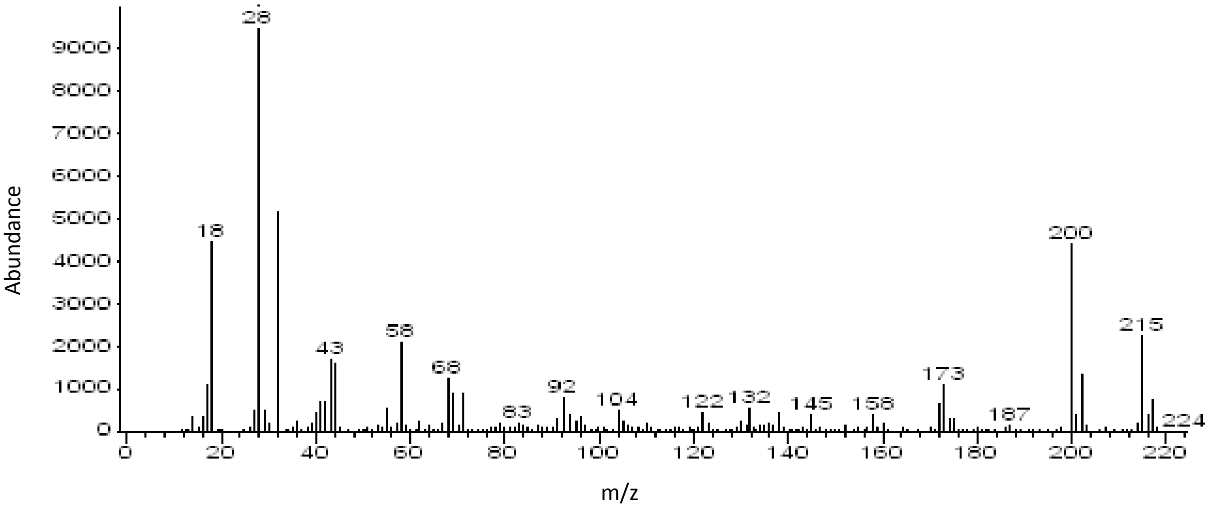


Figure 5.14: Mass spectrum of Atrazine extracted from pesticide-POCIS after a 32 day exposure in the Ringsend deployment site (October-November 2011)

Other compounds that were detected and identified with POCIS samplers include 2,6-dimethyl-heptadecane (CAS: 54105-67-8) which is used is a wide range of household, industrial and craft products, and Etorphine (CAS: 14521-96-1) which is a semi synthetic opioid which possesses an analgesic potency of 1000-3000 fold that of morphine. Etophine has found use in the immobilisation of large mammals, and is available legally only for veterinary use.

5.3.3.2 CHEMCATCHER

Four non-polar Chemcatcher were deployed for 32 days by the Ringsend Outflow pipe. Two priority pollutants were detected in the samplers; alachlor (Figure 5.15) and fluoranthene (Figure 5.16). These compounds were detected at concentrations of 0.66 µgL^{-1} and 0.85 µgL^{-1} respectively.

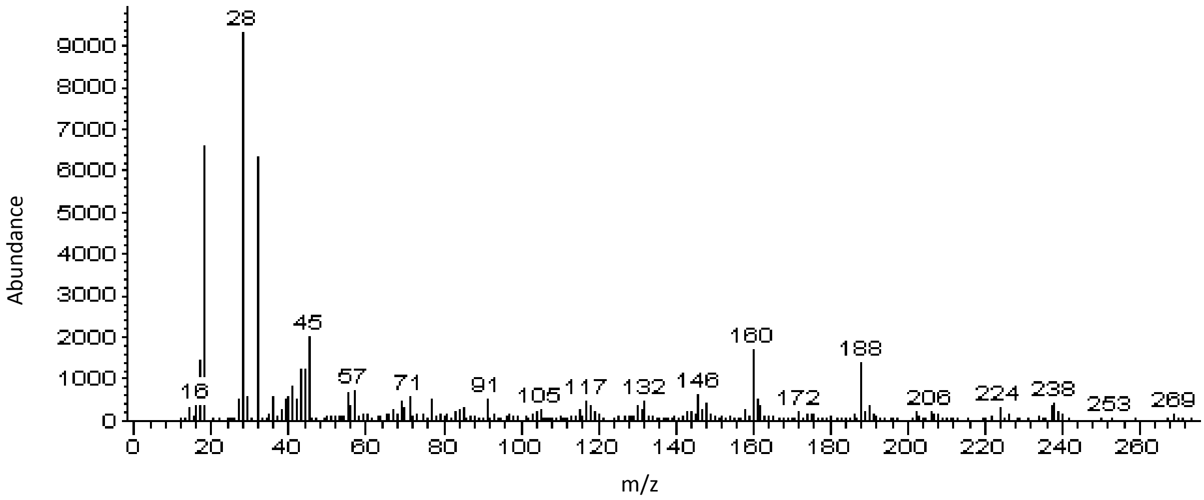


Figure 5.15: Mass spectrum of Alachlor extracted from non-polar Chemcatcher after a 32 day deployment in the Ringsend site (October-November 2011). GC-MS Method: Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min)

These levels fall far below the maximum allowed concentrations set by the EPA for both freshwater and marine waters, 0.7 µgL^{-1} for Alachlor and 1 µgL^{-1} for fluoranthene (137).

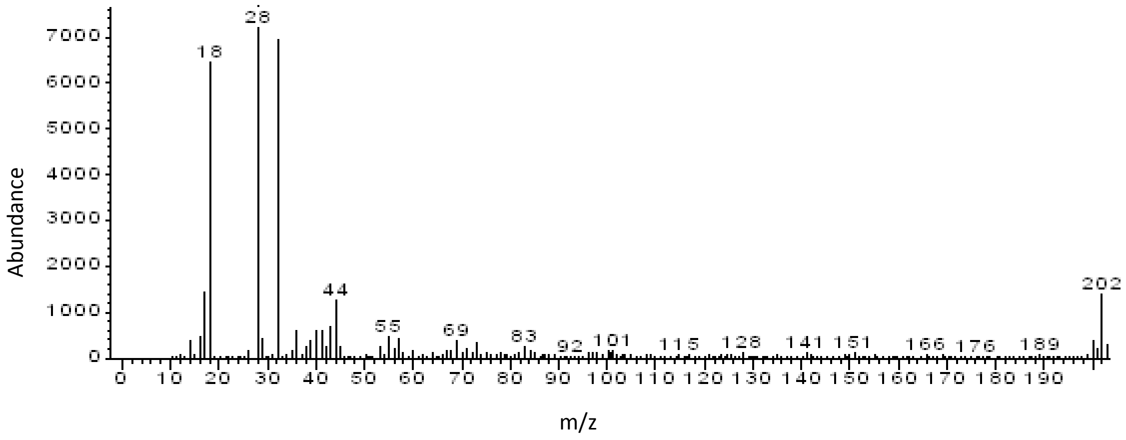


Figure 5.16: Mass spectrum of Fluoranthene extracted from non-polar Chemcatcher after a 32 day deployment in the Ringsend site (October-November 2011). GC-MS Method: Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min)

Some of the other compounds detected include Fluxetine (CAS: 54910-89-3) known commercially as Prozac. (27) Metanephrine (CAS: 5001-33-2) was also detected in the sampler extract. Metanephrine is a metabolite of epinephrine (CAS: 51-43-4) which is also known as synthesized adrenaline (28).

5.3.3.3 NOVEL PLASTICISED PASSIVE SAMPLING DISKS

Out of the five novel passive sampling disks (Table 5.1) deployed the only priority pollutant mentioned in the WFD that was detected was bis 2 ethyl hexyl phthalate (DEHP) (Figure 5.17). This pollutant was detected in both the ML and the BOP doped samplers

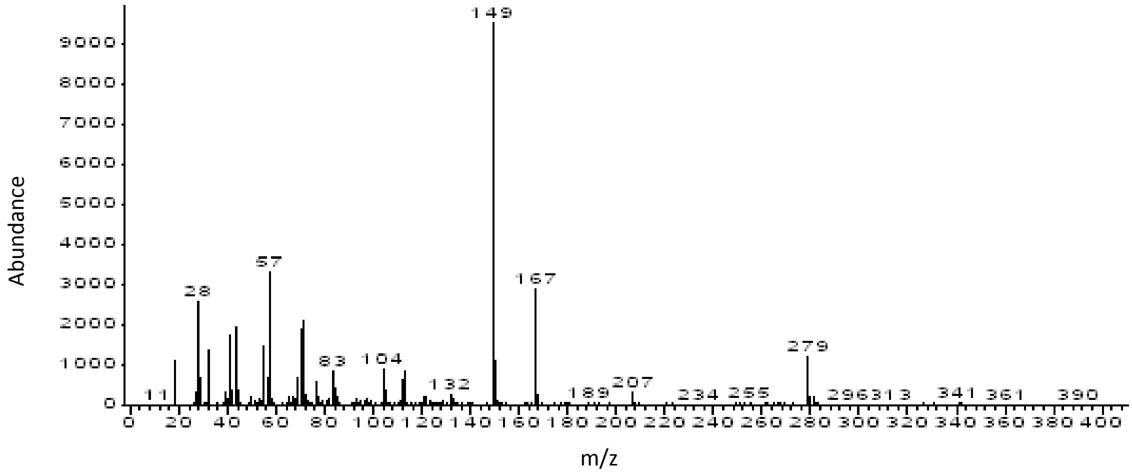


Figure 5.17: Mass spectra of DEHP obtained from DA doped passive sampler after a 32 day deployment in Ringsend (October-November 2011). GC-MS Method: Initial temperature 40°C (hold 2 min), 9 °Cmin^{-1} to 170 °C, 3 °Cmin^{-1} to 205 °C, 1°Cmin^{-1} to 208 °C, 20 °Cmin^{-1} to 290 °C (hold 2 min)

However one issue with the quantification of low levels of DEHP is that it is present as a contaminant in almost all laboratory equipment and reagents. DEHP has been found as a contaminant in plastics, glassware, aluminium foil, cork, rubber (29), Teflon sheets and solvents (30). Efforts have been made to reduce laboratory contaminations (31); however DEHP can still be detected in laboratory blanks. Low levels of DEHP were detected in blanks ran between samples, initially this was thought to be carry over from previous injections, however after injecting a series of seven blanks the level of DEHP was not seen to decrease. This indicates that the DEHP is present in the blank sample either through contamination from the septum of the GC vial, the vial itself or within the solvent bottle.

Other compounds that were detected include Sarkosyl (CAS: 1000128-73-6), also known as Sodium laurol sarcosinate, which is an ionic surfactant found in shampoos and shaving products as a foaming and cleansing agent, PMA a drug in the amphetamine mentioned previously. Another compound that was found in both the BOP and the DA doped passive samples is Fluoxetine (CAS: 54910-89-3) which is also known by the trade name Prozac, an antidepressant of the selective serotonin reuptake inhibitor class, and is approved for the treatment of major depression, obsessive compulsive disorder, and panic disorders (27).

5.4 CONCLUSIONS

Passive sampling devices were deployed in Ringsend for a eight month period of April to November 2011, and in Lough Hyne for a 1 month period in April 2011. The Ringsend site was selected in collaboration with GM-IT. Initially a third site was selected in Mutton Island, Co. Galway, however after initial deployment of samplers it was found that due to high winds and rough seas these samplers had been washed to sea. This was also an issue in Ringsend.

Out of the seven months of deployment in Ringsend, novel passive sampling disks were put out for five of these months. However, once the deployment period was over in three of these cases it was found that the sampling devices was not present at the site. At the deployment site, for the initial case of lost sampling devices (May-June 2011), it was determined that unlike the previous sampling period the sampler was not tethered sufficiently. For the next deployment (June-July 2011) even with the use of extra cable ties the same issue occurred and the sampler was lost at sea. It was then decided for extra security and to ensure adequate tethering of the cage containing the passive sampling devices, that the cage would be inserted into the bag containing the mussels to allow extra protection from the sea. One issue that was found with this was that the bag was still too full with the mussels to allow for addition of the sampling cage. For this reason during the deployment period of July-August 2011 no sampling devices were deployed in Ringsend. After this point samplers were deployed on a monthly basis for the next three months. During the period September-October 2011 when going to retrieve the samplers it was found that the bag containing both the mussels and the samplers had been removed from the water and emptied. As has been mentioned previously vandalism is a main issue that can arise during the deployment of passive sampling devices.

A significant difference can be seen between the two sites selected for the deployment of these devices. Lough Hyne is a site based in a rural setting where as Ringsend is based in an urban setting with influent coming from both household and industrial sources. This can be seen in the pollutants that were picked up in the two sampler sets for the month of April-May 2011. In the Lough Hyne site the only compounds that were detected were plasticisers, some of which can be attributed to leaching of the samplers, DMP and ML, themselves and possible degradation products. In comparison a series of pollutants were detected in Ringsend in all months including caffeine which was not detected in any of the samplers deployed in Lough Hyne. Caffeine has recently been studies to show the human impacts on aquatic systems. Once caffeine is consumed it is metabolized but a small percentage (0.5-10%) will not be metabolized and instead will be excreted intact. There have been cases where a link to elevated caffeine concentrations, as those seen in Ringsend over the sampling period, can be associated with high population densities (32).

Another finding that illustrates the difference between the rural and urban sites is the presence of pharmaceuticals detected in Ringsend. Desmethyldoxepin (CAS: 1225-56-5) a metabolite of Doxepin (CAS: 1688-19-5) (33) was detected in two out of the three sample periods analysed from Ringsend. Interestingly it was found that desmethyldoxepin, was not present in the samplers after the initial deployment (April-May 2011) but was in subsequent deployments (August-September 2011, October-November 2011). This follows previously published data (34) that stated the concentration levels of anti-depressants may be significantly high in autumn and winter which is considered a period of greater prescription.

When looking at the comparison of commercial samplers with the novel passive samplers developed in Chapter 3 that were deployed from the period of October-November 2011 atrazine, alachlor and fluoranthene, were detected through use of commercial passive samplers but not in the novel passive sampling disks. Atrazine was detected using the pharmaceutical-POCIS whereas both alachlor and fluoranthene were detected using the non-polar Chemcatcher. Whilst these three compounds were detected they were all detected at values at least 500 fold below that of the reported EQSs. These compounds were not detected in the developed passive samplers that were deployed during the same time frame. This could be due to lack of sensitivity of the novel passive sampling disks in comparison to the commercial passive samplers. This can be combated through use of longer deployment times of the novel passive sampling disks.

When looking at the deployed samplers it was noted that even with their deployment within the protective cages, both the POCIS and Chemcatcher passive samplers' accumulated large amount of sediment deposited on the limiting membranes in comparison to the novel developed passive samplers. From this it is possible to deduce that the pollutants detected by the commercial samplers could have accumulated within the sediment and then diffused into the receiving phase. Conversely though due to the fact that the developed samplers did not suffer this issue, and as was shown by the SEM image of the DA doped passive sampler very little bio fouling occurred. From keeping this in consideration these novel developed passive samplers may have greater potential as medium to long term samplers, in so much as reported sampling periods of Chemcatcher are in the region of 2 weeks to 1 month, and for POCIS deployment times have been reported for up to 2 months (2) but most commonly a 28-30 day deployment is published.

Passive sampling techniques show great promise in the field of water monitoring. Several disadvantages still can be seen, both chemical and the physical deployment of the samplers. Despite these issues great advantages can still be seen through the deployment of these devices. Due to the long term accumulation within the sampler, pollutants can be detected that may not be initially observed in a grab sample, as was seen with atrazine, alachlor, and fluoranthene. This can be explained due to the volume of water that is sampled by the passive sampler which will vary with sampling rates calculated for individual pollutants. Passive samplers will give a TWA concentration of these analytes which will allow for any episodic events that could be missed by grab sampling.

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CHAPTER 6: CONCLUSIONS

The aim of this thesis was to develop a novel cost effective passive sampling device that could be used to detect pollutants in surface water. This work was carried out based on the recommendation of the WFD for improvements in aquatic monitoring methods. Currently used methods for this involve grab sampling, which is ineffective both in terms of cost and time.

Initial work in this thesis was carried out by researching the literature. Passive sampling technologies has been reported for many years, however it is only in the last two decades that interest has expanded from air passive sampling to include aquatic passive sampling. Further on from this (Chapter 2) a series of methods were developed based on previously used methods for the analysis of pollutant samples.

It was important to develop and test a SPE method for not only the clean up but also pre concentration of a series of grab samples that were taken during the duration of the project. Two sites were sampled; The River Tolka (February 2008) and Ringsend (April-November 2011). The initial sample was taken to ensure that the analytic methods developed were fit for their purpose. In this sample DEHP was the only priority pollutant detected. As has been mentioned earlier there are a series with issues in the quantification of DEHP as it is present as a contaminant in almost all laboratory glassware.

Alongside the SPE method two other analytical techniques are presented for the analysis of the pollutants. It was important to have a rapid determination method for the testing of the novel passive sampling devices where unlimited access to the instrument was possible. For this a HPLC method was developed (Section 2.3.3) initially for the determination of two compounds, atrazine and dieldrin. This method had a run time of 8 min which allowed for the screening of the novel passive samplers at regular time intervals in the enrichment studies. A second analytical method was developed for the determination of pollutants in both surface water and the novel passive samplers after deployment periods. The method was developed on a GC-MS that was available in the School of Chemical Sciences (DCU) and had a MS library that could be used to aid in the identification of unknowns that were detected within these samples (Section 2.3.2). This method had two disadvantages over the HPLC method. The run time was much longer (40 min) and there was limited time available on the instrument as it was communal. For this reason the method was not used as regularly as the HPLC method. An advantage it had over the more regularly used HPLC method was the sensitivity it imparted on analysis both in TIC and SIM mode.

Within Chapter 3 the development of these novel passive samplers is detailed. Two protypes were developed. Initially work was carried out on glass mounted passive samplers (Section 3.3.1). These were tested within laboratory conditions and showed promise. One issue that was related to them however was in which way they could be deployed within the environment. When deployment times within the laboratory exceeded 1 week the films started to detach from the glass slides, and with longer deployments would become fully detached. Keeping this in consideration a second prototype was developed – the novel passive sampling disk (Section 3.3.2). This disk was cast with the dimensions 21 mm x 0.2 mm and could be deployed into the environment through suspension with string.

Initial work was carried out using diisononyl adipate as a plasticiser as this had showed favourable results for a range of Log K_{ow} (2.6-5.4). This range encompassed the majority of pesticides that were mentioned in Annex X of the WFD. Studies were carried out using this configuration of the novel passive sampling device to study the enrichment of analytes in both single and multi component systems. From this a model was developed to show the prediction of kinetic sampling rates. The model was based on the Log K_{ow} of the pollutant against a calculated rate constant. From this model experimental values of concentration values for two pesticides, diuron and trifluralin, were shown plotted against the predicted value (Figure 3.14). Good correlation of these two series were noted for both compounds.

Furthering on from this work a study was undertaken to determine if a selective novel passive sampler could be developed. A series of 29 plasticisers were tested against three compounds (atrazine, dieldrin and fluoranthene). It was found that while a plasticiser could not be determined for selective determination of the more non polar compounds e.g. dieldrin and fluoranthene, one configuration of the sampler (tricapryl trimellitate) showed selectivity for the polar compounds (lower Log K_{ow}).

Fickian diffusion had been noted in the diffusion curves obtained with the work from Chapter 3 and work had been previously done on the determination of the diffusion coefficient based on ATR measurements. A series of compounds were selected for IR study (Section 4.3.1). A main advantage of using IR to determine diffusion coefficients is the rapid determination in which samples can be obtained. From this it is possible to generate a large volume of data points which in turn will aid in the accurate determination o f the diffusion coefficient.

Initially the enrichment of six pollutants into the novel polymeric material was studied and A_t/A_{eq} was plotted against time. It was observed that a Fickian diffusion curve was obtained. From this curve two values were obtained, T_{90} and T_{100}. The values obtained for T_{90} and T_{100} were plotted against the Log K_{ow} of the pollutants to determine if any correlation could be established. In both cases a third order polynomial curve was obtained. To test the accuracy of this prediction curve a forth pollutant (anthracene) was studied experimentally and values for both T_{90} and T_{100} were established. When these experimental values were compared to the predicted values it was observed that %RSD of 0.1% and 8.4% were obtained for both values respectively.

A Matlab script (Appendix I) was written by Nina Hanzlikova to calculate D from Eqn. 4.4 using experimental values obtained for the tested pollutants (Section 4.3.2.2) which were found in the range of 1.4×10^{-9} to 5.9×10^{-9} cm^2sec^{-1}. Using a series of chemical and physical properties of the pollutants it had been hoped that a model to predict the diffusion coefficient could be obtained. However, this was not the case due to the fact that it is not just water solubility, molecular weight and molecular radius that will affect the diffusion of a pollutant into the polymeric material but also the steric effects of the penetrant into the material and properties of the polymeric material itself.

While the work on the project was largely based within the laboratory it is important to carry out field trials for the samplers. Two sites were selected to deploy the novel passive sampling devices; Loch Hyne and Ringsend. The results from Loch Hyne showed no priority pollutants or pharmaceuticals within the water. This was expected based on its rural setting in comparison to Ringsend. Initial deployment in Ringsend was of the novel passive samplers alone. During this period (April-October 2011) whilst no priority pollutants (with the exception of DEHP) were detected a series of other pharmaceuticals and higher alkanes were.

For the last deployment the novel passive samplers were deployed alongside three commercial passive samplers; two POCIS configurations and Chemcatcher samplers (Section 5.3.3). After analysis of these samplers it was found that three priority pollutants were detected in the commercial samplers; atrazine in pharmaceutical-POCIS, and alachlor and fluoranthene in non-polar Chemcatcher. These compounds were detected at concentrations almost 500 fold under the max allowable concentrations set down.

One recommendation that would arise from this project is that through use of plasticisers that exhibit antifouling properties e.g. diisononyl adiapte (Figure 5.9) it is possible to decrease the biofilm that will occur on these passive samplers. Whilst the novel passive samplers developed within this project did not display the same sensitivity as those commercially available they did show one large advantage. Due to the shape of both the POCIS and the Chemcatcher samplers there is an indent for the limiting membrane. During the deployment study undertaken it was found that a large volume of sediment remained deposited in this area. This was despite the fact that both samplers were deployed within protective cages. In comparison the novel passive samplers do not have this indent as they are simply a flat disk. Due to this a build up of sediment was not observed. The recommendation that would be given is that these novel passive samplers display the ability for longer deployments (> 1 month) and in doing so this would decrease the disadvantage displayed by the low sensitivity.

The novel passive samplers developed within this project can be made inexpensively and are not time consuming to produce. Due to the use of the polymeric material the plasticiser used can easily be altered to convey either extra antifouling properties for long term deployments or selectivity for highly water soluble pollutants.

APPENDIX 1: MATLAB SCRIPTS

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%   Curve fit to calculate diffusion constant from                    %
%    from experimental measurements of absorbance                     %
%              Author: Nina Hanzlikova                                 %
%           (nina.hanzlikova2@mail.dcu.ie)                            %
%                November 2011                                         %
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
function output= diffusion_fit(params,Input,Actual_Output)
a=params(1);
% Set d_p and L to experimentally measured values here (for calculation)
% and in diffusion_fit.m
d_p = 0.0001338;;
L = 0.00442;
const1 = 8./(pi.*d_p.*(1 - exp(-2.*L/d_p)));
% set number of elements in summation here and in diffusion_calc.m
size_sum = 10;
n = ones(size_sum, size(Input));
ind = find( ones(size_sum, 1) );
ind = ind - 1;
sum_part = zeros(size(Input), 1);
for j = 1: size(Input)
   n(:,j) = (exp(-a.*(2.*ind+1).^2.*pi.^2.*Input(j)/(4*L^2))..
```

```
        .*( (2.*ind + 1).*pi./(2.*L).*exp(-2.*L./d_p) + (-1).^ind.*(2./d_p)))..

        ./( (2.*ind + 1).*(4./d_p.^2 + (2*ind + 1).^2.*pi.^2/(4*L.^2)));

    sum_part(j) = sum(n(:,j));

end

Fitted_Curve = 1 - const1.*sum_part;

Error_Vector=Fitted_Curve - Actual_Output;

% When curvefitting, a typical quantity to

% minimize is the sum of squares error

output=sum(Error_Vector.^2);

% You could also write sse as

% sse=Error_Vector(:)'*Error_Vector(:);
```

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
 %   Curve fit to calculate diffusion constant from                                  %
 %    from experimental measurements of absorbance                                   %
 %            Author: Nina Hanzlikova                                                %
 %          (nina.hanzlikova2@mail.dcu.ie)                                           %
 %               November 2011                                                       %
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%


[input1, input2] = textread('Absorption.dat','%f %f');
% Put data in Absorption.dat in form 't A_t/A_eq'
t = [input1];
A_tA_eq = [input2];


Starting=[1e-7];
options=optimset('Display','iter');
Estimates=fminsearch(@diffusion_fit,Starting,options,t,A_tA_eq)
% To check the fit
figure;
plot(t,A_tA_eq,'*')
hold on
% set d_p and L to actual measured parameters here (for plotting) and in
% diffusion_fit.m (for calculation).
```

```
d_p = 0.0001338;

L = 0.00442;

const1 = 8./(pi.*d_p.*(1 - exp(-2.*L/d_p)));

% set number of elements in summation here and in diffusion_fit.m

size_sum = 10;

n = ones(size_sum, size(t));

ind = find( ones(size_sum, 1) );

ind = ind - 1;

sum_part = zeros(size(t), 1);

for j = 1: size(t)

   n(:,j) = (exp(-Estimates(1).*(2.*ind+1).^2.*pi.^2.*t(j)/(4*L^2))..

      .*( (2.*ind + 1).*pi./(2.*L).*exp(-2.*L./d_p) + (-1).^ind.*(2./d_p)))..

      ./( (2.*ind + 1).*(4./d_p.^2 + (2*ind + 1).^2.*pi.^2/(4*L.^2)));

   sum_part(j) = sum(n(:,j));

end

curve2 = 1 - const1.*sum_part;

plot(t, curve2, 'r')
```