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Passive Sampling for Quality Monitoring of Irish Marine Waters

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Abstract

This study details the steps involved in fabrication, deployment and retrieval of mainly polydimethyl siloxane (PDMS) passive sampling devices deployed in a number of locations in and around Ireland in an attempt to derive dissolved water concentrations of contaminants *in-situ*. PDMS samplers were initially deployed in the Burrishoole catchment, Co. Mayo in conjunction with the collection of biological tissues and sediment to investigate the source of elevated dioxins in the catchment. Passive samplers were used to generate dissolved water concentrations of persistent organic pollutants (POPs) and also to successfully screen for the presence of dioxins in the water column. The dioxin profile present was also found in sediment and biological tissue and through statistical profiling potential sources were identified as being possibly related to the use of technical pentachlorophenol in the catchment though no direct evidence was found.

Passive samplers (PDMS and SPMD) were then deployed at various depths on the M6 weather buoy, 400 miles off the West Coast of Ireland, in conjunction with temperature and salinity monitors to test how the technology would fare over a long period deployment (585 days) in a harsh, dynamic environment. The PDMS samplers were almost completly lost where the SPMDs last better (80 % recovered). Dissolved water concentrations estimated using both sampler types were found to be very low (<ppb) with polyaromatic hydrocarbons found in higher levels than polychlorinated biphenlys, and organochlorine compounds. The use of statistical analysis suggests that passive samplers can also be used to differentiate different water masses by investigating contaminant loadings at each depth sampled.

Finally passive samplers were deployed in various inshore and inland waters across Ireland with the results indicating that the remote West of Ireland had the lowest levels of dissolved water concentrations estimated. Many estuaries and inland water bodies had levels of contaminants higher than the west of Ireland with the heavily industrialised Cork and Dublin sites having the highest levels estimated. The separation of sites based on concentrations found indicated that assessment criteria could be generated in an Irish context (IRef) which could be used to classify a site in relation to 'background' levels found in the West of Ireland and at M6.

The results generated during this study were then assessed based on various legislative requirements and assessment criteria such as the Water Framework Directive (WFD) and the Oslo Paris convention (OSPAR). Results from the WFD assessment indicate that concentrations found at all sites were below the EQS values set down. However this EQS value is based on total water concentration hence the EQS was modified to a dissolved water concentration basis. This reduced the total water EQS values by up to 80 % for some analytes however in most locations the dissolved water concentrations found were at or below this dissolved water EQS value indicating that the levels of contaminants from across Ireland are below the EQS values generated as part of the WFD. Assessments were also made on the concentrations found across Ireland using background assessment criteria (BAC) suggested by OSPAR. The results indicate that the levels across Ireland are above the BAC for most compounds with the M6 weather buoy faring better. Concentrations from "pristine" Irish sites were then chosen to generate reference criteria on an Irish basis (IRef) which were found to be below the concentration levels suggested as part of the BAC assessment criteria in the majority of locations.

Authors Declaration

I certify that this thesis which I now submit for examination for the award of Doctor of Philosophy, is entirely my own work and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my own work.

This thesis was prepared according to the regulations for postgraduate study by the research of the Dublin Institute of Technology and has not been submitted in whole or in part for an award in any other Institute or University.

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Scope of Thesis

Contaminants, many anthropogenic in origin, are released into the environment through a variety of means. Many of these compounds are toxic and bio-accumulative in nature and can persist for long periods in the environment. There is much concern amongst environmental scientists in regards to these chemicals and their fate in the environment. The Water Framework Directive (WFD) (2000/60/EC) produced a legislative requirement to monitor and attempt to improve the quality of waters across Europe by 2015. To this end water bodies from across Europe were broken down into river basin districts including coastal and transitional waters, each of which requires monitoring and surveillance to assess the quality of water present. The WFD has identified a list of priority and relevant contaminants which must be measured if 'good ecological and chemical status' is to be achieved by 2015.

The WFD does not specify the means by which these waters are to be monitored however 'spot' water sampling is accepted as the general technique of choice. This technique, though accepted for monitoring and legislative requirements, has many drawbacks inherent in its design. Primarily 'spot' water sampling provides a 'snapshot' of the environment at the time of sampling and may miss point source impacts or seasonal and spatial changes in water composition. With 'spot' water sampling sensitivity is often a challenge as compounds are present in very low concentrations in the water column hence large volumes are required which means the additional problem of transportation not to mention exhaustive laboratory work. The concentrations of contaminants present in the water column are generally sorbed to the particulate matter present which has consequences for correct concentration assignment.

Many environmental monitoring programmes also employ the use of bio-monitor species or analysis of sediment to augment 'spot' water sampling however these techniques are problematic in trying to achieve an overall assessment of water quality in that accumulation of contaminants in an organism is reliant on species, health status, size, sex and growth rate. Passive samplers are a technology which offers the chance to estimate dissolved water concentrations of contaminants at very low concentrations (sub ppb) which can take into account point source impacts, temporal and spatial trends. They are simple to deploy and have been found to be robust in the environment. Extraction and analysis of these devices has also proven to be a straight forward procedure with the use of performance reference compounds providing *in-situ* calibration. Finally the truly dissolved water concentrations of contaminants provided by PS is thought to be the most relevant to the environmental scientist and though not currently relevant directly to satisfy legislative requirements, including the WFD, can be used as an important tool in understanding the status of the marine environment. This study builds on existing literature where the theory and concepts of PS are widely reported. In particular this study focuses on trialling and measuring the applicability of known concepts in the field using ongoing and developing technologies. This is achieved through the deployment of PS devices in three field investigations (Chapters 4, 5 & 6), with the ultimate aim of assessing the possibilities of using PS for regular environmental monitoring programmes in Ireland.

Chapter 1 identifies that there is a gap in environmental monitoring programmes which can be filled using passive sampler technology. It sets out the various legislative requirements along with details of contaminants monitored over the course of this study. Finally chapter 1 discusses the potential of using passive samplers to satisfy the Water Framework Directive.

Chapter 2 discusses the theory of passive sampler design and operation in the environment. It illustrates the method by which samplers sequester contaminants from the environment and the drawbacks in passive sampler design. This chapter also discusses the use of performance reference compounds and the choice of passive sampler used in this study.

Chapter 3 shows the method development and validation of techniques used to monitor contaminants in various environmental compartments including biological tissue and sediment as well as passive samplers. It details the chromatographic set up for contaminant analysis as well as all aspects of quality control.

Chapter 4 is a case study where passive samplers were used in conjunction with biological tissue and sediment to attempt to elucidate a potential point source influence in relation to elevated levels of dioxins found in eels in the remote Burrishoole catchment in Co. Mayo. In addition to screening for Dioxins (PCDD/Fs) and polychlorinated dipehnyl ethers (PCDEs) in the water column this chapter also illustrates the importance of an integrated monitoring assessment, including passive samplers and statistical analysis in elucidation of point source impacts.

Chapter 5 details the deployment, recovery and analysis of passive sampling devices at the M6 weather buoy which is approximately 400 miles off the Irish west coast in deep water (3000 m). This location is at a confluence of different Atlantic water masses each with its own chemical inputs. Passive samplers were used to attempt to differentiate these water masses in conjunction with regular nutrient and temperature measurements. This work was deemed as valuable in terms of the unique attributies of the site

investigated and also in the accumulation of offshore data for POPs where few such data (especially for PBDEs) are currently available in such ‘pristine’ sites.

Chapter 6 illustrates the potential use of passive samplers in routine monitoring programmes with samplers deployed in 24 locations around the country including inshore and freshwater locations. The data generated was used to assess the dissolved water concentrations from all sampled sites. Statistical analysis was completed on the data generated which was then used to show the differences in pollutant loadings in each different water type sampled along wth the importance of estimating the contribution of the salting out effect on the estimation of final dissolved water concentrations.

Chapter 7 takes the data generated throughout this study, from various locations and assesses the water quality under various legislative and monitoring requirements including the WFD and OSPAR assessment criteria as well as the Irish Reference background assessment criteria (IRef). This chapter also illustrates that passive samplers can be used in routine monitoring programmes and can be used to fill gaps in the existing monitoring programmes of many countries and further, can be used to satisfy legislative requirements including the WFD.

Abbreviations

BAC	Background Assessment Criteria
BAF	Bio-Accumulation Factor
BFR	Brominated Flame Retardants
BIOTA	Biological Tissue
CEMP	Coordinated Environmental Monitoring Programme
CRM	Certified Reference Material
DDT	Dichlorodiphenyltrichloroethane (Pesticide)
DDE	Dichlorodiphenyldichloroethylene (Pesticide)
DGT	Diffusive Gradients in Thin films
DOC	Disolved Organic Carbon
D W	Dry Weight
EDC	Endocrine Disrupting Compound
ENAW	Eastern North Atlantic Water
EPA	Environmental Protection Agency
EQS	Environmental Quality Standard
ERGO	ERGO Laboratories, Hamburg, Germany
EU	European Union
Fg	Femtogram
GES	Good Environmental Status
GC-ECD	Gas Chromatograph Electron Capture Detector
GCMS	Gas Chromatography Mass Spectrometry
HCB	Hexachlorobenzene (Pesticide)
HCH	Hexachlorohexane
HOC	Hydrophobic Organic Compounds

HPLC	High Pressure Liquid Chromatography
ICES	International Council for the Exploration of the Sea
JAMP	Joint Assessment and Monitoring Programme
LDPE	Low Density Polyethylene
LOD	Limit of Detection
LSW	Labrador Sea Water
LOQ	Limit of Quantitation
MCWG	Marine Chemistry Working Group
MSFD	Marine Strategy Framework Directive
MI	Marine Institute
MW	Mediterranean Water
NEAD W	North East Atlantic Deep Water
NORMAN	Network of Reference Laboratories And Related Organisations
ng	Nanograms
NIOZ	Royal Netherlands Institute for sea research
NIVA	Norwegian Institute for sea research
NWA	North West Atlantic
OCDD	Organochlorine Diphenyl-p-dioxin
OC	Organochlorine Compound
OSPAR	Oslo Paris Convention
PAH	Polyaromatic Hydrocarbons
PBDE	Polybrominated Diphenyl Ethers
PCA	Principal Components Analysis
PClA	Pentachloroanisole
PCP	Pentachlorophenol
PCB	Polychlorinated Biphenyls

PCDD	Polychlorinated Dibenzo-p Dioxin
PCDD/F	Polychlorinated Dibenzo-p-Dioxin/Furan
PCDE	Polychlorinated Diphenyl Ether
PD	Passive Dosing
PDMS	Polydimethylsiloxane
PFOS	Polyflourooctane sulfonate
POCIS	Polar Organic Chemial Integrative Sampler
POM	Polyoxymethylene
POP	Persistent Organic Pollutant
PS	Passive Sampling
PSD	Passive sampling Device
PSTS	Passive Sampling Trial Survey (2007)
PRC	Performance Reference Compounds
QUASIMEME	Quality assurance of information for the marine environment
SAIW	Sub-Arctic Intermediate Water
SCICOM	Steering Group on Human Interactions and Ecosystems
SEC	Shelf Edge Current
SIM	Single Ion Monitoring
SPM	Suspended Particulate Matter
SPMD	Semi-permeable Membrane Device
TCDD	Tetra Chlorinated Dibenzo-p-Dioxin
TWA	Time weighted average
UCM	Uncertainty of Measurment
US	United States of America
USGS	United States Geological Survey
VOC	Volatile Organic Compound

WFD	Water Framework Directive
WKPSPD	Workshop on Passive Sampling and Passive Dosing
WBL	Water Boundary Layer
W W	Wet Weight

TABLE OF CONTENTS

List of Tables and Figures

Chapter 1: Environmental Monitoring of Persistent Organic Pollutants: Setting the Context

1.1 Monitoring Programmes for the Marine Environment

The marine environment can be subject to anthropogenic pollution from a variety of sources including from industrial and agricultural processes, atmospheric deposition and sewage wastewaters. Many of the compounds released from pollution of this type can be resistant to environmental degradation and so can persist in the environment for long periods, comprising many years or decades, and in many cases are toxic to the marine organisms present. Poor environmental management can compound this problem by further allowing many contaminants, which can have detrimental effects on human health and wellbeing to enter the food chain.[1]

Marine pollution, is defined by OSPAR as "the introduction by man, directly or indirectly, of substances or energy into the maritime area which results, or is likely to result, in hazards to human health, harm to living resources and marine ecosystems, damage to amenities or interference with other legitimate uses of the sea" [1] The EU further define pollution as "the direct or indirect introduction, as a result of human activity, of substances or heat into the air, water or land which may be harmful to human health or the quality of aquatic ecosystems or terrestrial ecosystems directly depending on aquatic ecosystems, which result in damage to material property, or which impair or interfere with amenities and other legitimate uses of the environment". [1]

In a wider context environmental monitoring focuses on the gathering of information that allows authorities to assess the quality of the environment, to identify possible threats posed by human activities and to assess whether earlier measures have been effective. Monitoring under the Marine Strategy Framework Directive (MSFD) has been further defined as the systematic measurement of biotic and abiotic parameters of

the marine environment, with predefined spatial and temporal schedule, in order to produce datasets that can be used for application of assessment methods and derive credible conclusions (with defined confidence) on whether Good Environmental Status (GES) is achieved or not for the marine area concerned. [2]

Following on from this, it is clear that monitoring programmes must carefully consider the choice of the parameters to measure, appropriate sampling sites and test media, temporal elements to sampling, sample handling and ultimately the accurate quantification of parameters in the selected media. Herein lie the challenges to both the environmental manager and the analytical chemist with respect to the design, data generation and assessment of monitoring programmes.

The importance of monitoring water quality has been recognised both nationally and within the European Union (EU) and has led to the introduction of various legislative requirements including those encompassed under the Oslo Paris Convention (OSPAR) [3] the Water Framework Directive (WFD) [4] and now more recently in support of Marine Strategy Framework Directive (MSFD, 2008/56/EC) objectives.[5] These have ultimately been introduced in order to ensure monitoring of the levels of POPs in the environment and to prevent priority pollutant levels from increasing.

Overviews of marine monitoring programmes are well described.[1,6] It is not the intention of this review to give an exhaustive overview of all active monitoring programmes thus only programmes directly relevant to the monitoring of organic persistent pollutants in the North East Atlantic and Irish waters including the Water Framework Directive (WFD) [4], the Shellfish Waters Directive (SWD)[7], Oslo Paris convention (OSPAR) [3] and the associated Joint Assessment Monitoring Programme

(JAMP) [8] as well as the Marine Strategy Framework Directive (MSFD)[5] are discussed in greater detail.

1.1.1 Oslo and Paris Convention

During the 1960s and early 1970s a number of pollution events in the North-East Atlantic Ocean provided the impetus for governments in the region to enact legislative restrictions on dumping. In 1972 the Oslo convention was signed, which was enacted to control and regulate dumping at sea, and entered into force in 1974.[9] Further to this the Paris convention dealt with pollution of the marine environment from land based sources and in 1978 it also came into force.[3] The existing Oslo and Paris conventions did not adequately control some of the many sources of pollution. In 1992 a new convention for the protection of the marine environment of the North-East Atlantic, OSPAR, was enacted entering into force in 1998.[9] OSPAR then established the Joint Assessment and Monitoring Programme (JAMP) [8] and the Coordinated Environmental Monitoring Programme (CEMP) [10] to better define common approaches to the collection of samples, the range of priority pollutants to be monitored, the generation of analytical data and in the preparation of assessments of the marine environments.[8]

OSPAR works under its Hazardous Substances Strategy to identify which substances are hazardous for the marine environment, to prevent, reduce and ultimately eliminate pollution with these substances, and to monitor the effectiveness of measures to achieve this. OSPAR ultimately seeks to move towards the cessation of discharges, emissions and losses of hazardous substances by 2020 with the ultimate aim to achieve concentrations of hazardous substances in the marine environment near background values for naturally occurring substances and close to zero for man-made substances.

A variety of hazardous substances have been prioritised for action by OSPAR due to their risk to the marine environment and which are being monitored under the Coordinated Environmental Monitoring Programme (CEMP).[10] CEMP monitoring is mainly focused on coastal areas because, in many cases, the response of the ecosystem to pollution control measures can best be assessed at locations close to discharge and emission sources. Increasing attention is being paid to monitoring in offshore areas, where a number of human activities (*e.g.* oil and gas production, shipping) take place and since the awareness of the significance of long-range transport of contaminants has increased. CEMP monitoring does not extend to deeper waters however the application of passive sampling in monitoring dynamic open water environments is incorporated into this thesis (Chapter 5).

The CEMP is underpinned by an emphasis on commonly agreed monitoring guidelines and quality assurance procedures and is currently being extended to include brominated flame retardants, dioxins and PFOS.[10] Contamination by cadmium, mercury, lead and selected PAHs and PCBs are assessed by monitoring concentrations in fish, shellfish and sediments. CEMP monitoring is designed to track contaminants which accumulate in the marine environment and through the food chain but which cannot necessarily be detected in seawater. Therefore CEMP assessment results may lead to different conclusions about chemical quality status than water-based monitoring under the EU Water Framework Directive. The OSPAR CEMP provides tested, quality assured methodologies for environmental monitoring that can contribute to the evaluation of good environmental status under the EU Marine Strategy Framework Directive and good chemical status under the Water Framework Directive.

Ireland is a contracting party to JAMP [8] in order to evaluate the status and trend of concentrations of hazardous substances in the marine environment and reports concentration data to national databases and then onwards to the International Council for the Exploration of the Sea (ICES) on an annual basis. Data are then further disseminated to the EU and other authorities.

Currently organic contaminant levels are monitored for OSPAR purposes in suitable bio-monitor organisms such as mussels and in sediments (see chapter 2). Passive sampling is however being incorporated into the OSPAR framework with monitoring data now being reported ultimately to be used in the generation of background concentrations of priority pollutants and associated assessment criteria.

1.1.2 Water Framework Directive

The Water Framework Directive (WFD) was transposed into Irish law by the European Communities (water policy) regulations in 2003.[11] The WFD is an important piece of legislation in that it aims to achieve and ensure good water quality across Europe by 2015. This is to be achieved by implementing management plans at a river basin level and monitoring is required to cover a number of 'water quality elements' including physicochemical properties, (which includes physical measurements such as temperature and density) hydromorphological status, (erosion and bench river characteristics), biological (distribution and composition of species and biological affects) and chemical monitoring (emphasises contaminants and priority pollutants).[12]

Three modes of monitoring regime are specified in the directive including:

- Surveillance monitoring aimed at assessing long term water quality changes and providing baseline data on river basins allowing the design and implementation of other types of monitoring;
- Operational monitoring aimed at providing additional and essential data on water bodies at risk of failing environmental objectives of the WFD;
- Investigative monitoring aimed at assessing the causes of such failure.

The marine environment is a complex ecosystem and as such a suitable set of 'tools' is required in order that surveillance monitoring will be adequate in assessing long term water quality changes and the data obtained is reliable and fit for purpose.[13,14]

The WFD has identified a new expanding list of priority and relevant pollutants with a requirement for substantial monitoring of these pollutants in transitional and coastal waters to achieve "good ecological and chemical status" by 2015, [12] by all Member States.

Further to this the European Parliament issued a new Directive in 2008 (Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008) on environmental quality standards in the field of water policy. Directive 2008/150/EC lays down the environmental quality standards (EQS) in accordance with the provisions and objectives of Directive 2006/60/EC. The annual average (AA) EQS and maximum allowable concentrations (MAC) expressed as µg/L have been defined for inland surface waters and other surface waters. It is a significant challenge to achieve sufficiently low detection limits to measure some priority substances at environmentally relevant concentrations and thus determine compliance with EQSs.

The WFD does not mandate the use of a particular set of 'tools' to meet the demands of these objectives but aims to ensure that those systems used to provide monitoring would comply with the quality elements mentioned in the WFD. With regards to chemical monitoring under the WFD, the method currently requested under legislation is that of spot water sampling followed by instrumental analysis or online continuous monitors. Emerging methods for this purpose include electrochemical sensors, immunoassays, biosensors and passive samplers. A potential role for passive samplers in WFD compliance will be discussed in greater detail in Chapter 2.

1.1.3 Marine Strategy Framework Directive

The aim of the Marine Strategy Framework Directive (MSFD) [5] is to protect more effectively the marine environment across Europe and attempt to establish a framework in which member states shall take necessary measures to achieve or maintain good environmental status in the marine environment by the year 2020. The directive provides legislation requiring member countries to adopt methodological standards for the assessment of the marine environment in line with directive 2007/2/EC of the European parliament,[5] establishing an infrastructure for spatial information across the EU. The MSFD requires all Member States to complete an Initial Assessment (Article 8), determination of Good Environmental Status (GES) (Article 9) and establishment of environmental targets and associated indicators (Article 10).

The MSFD Task Group 8 (TG8) state that within descriptor 8 under the MSFD, three core elements of data assessment are recommended:

- Concentrations of contaminants in water, sediment and/or biota are below environmental target levels identified on the basis of ecotoxicological data;
- Levels of pollution effects are below environmental target levels representing harm at organism, population, community and ecosystem levels;
- Concentrations of contaminants in water, sediment and/or biota, and the occurrence and severity of pollution effects, should not be increasing.

TG8 further recommends that monitoring programmes should include the assessment of concentrations of contaminants in environmental matrices, *i.e.* water, sediment, and the tissues of biota.

As per the WFD it is evident that passive sampling may, in conjunction with other techniques, potentially offer a direct measure of the concentration of active contaminants present in the water and sediment of a treaty area.[15] POPs relevant to the scope of this study are further discussed below, while current Irish monitoring programs are described in detail in Chapter 2.

1.1.4 Current Monitoring Tools

The Marine Institute carries out monitoring and research and in the provision of environmental advice specifically focused on the assessment of the extent and impacts of pollution and to determine environmental trends.[16] Two broad groups of chemical pollutants are of concern for the marine environment namely, nutrients and hazardous substances. The Marine Institute (where this research was completed) carries out

monitoring and research in relation to these. Hazardous Substances and specifically with respect to this research (*i.e*. organic substances) are of concern due to their environmental persistence (resistance to degradation), toxicity and ability to bioaccumulate, *i.e*. accumulation in the tissue of organisms.

As described previously there are many national and international (European and global) instruments and conventions designed to protect the marine environment from pollution. Of particular relevance to Ireland is EU law and also the 1992 OSPAR Convention for the Protection of the Marine Environment of the North East Atlantic and more recently in support of the WFD and SWD.[7,11]

OSPAR provides a framework in which the riparian states of the NE Atlantic work together to protect the marine environment from adverse effects of human activities and to conserve marine ecosystems. Monitoring and assessment of marine environmental quality is implemented to comply with various EU directives (*e.g.* WFD) and also in accordance with OSPAR's Joint Assessment and Monitoring Programme.

Specific Marine Institute monitoring and research activities include:

- Measurement of contaminants to support protection of shellfish growing areas,
- Measurement of contaminants to support protection of the consumer of fisheries produce,
- Determination of trends and concentrations of winter nutrient levels in the Irish and Celtic seas,
- Determination of levels, temporal trends and effects of hazardous substances in the Irish marine environment,
- Pollution measurement in support of the WFD (multi matrix measurements including passive sampling),

- Integrated levels and effects assessments of contaminants in the marine environment,
- other supporting research.

A variety of measurement techniques are employed in order to complete analytical measurements, some of which are briefly discussed below.

1.1.4.1 Analysis of Seawater

WFD EQS have been developed for the most part for water as more information is available to develop EQS for water and it provides a measurement of current status.[17] EQS are set for metals on a dissolved water basis and for other substances the EQS is set in total waters. For many substances of concern in the marine environment, *i.e.* POPs, water monitoring presents difficulties as, analytical challenges can arise due to salt interference, from contamination or due to the difficulty of detecting many low solubility substances at environmentally relevant concentrations, the variability can be spatially and/or temporally high in tidal waters necessitating high frequency sampling which can be prohibitive in sample acquisition and analytical costs.

1.1.4.2 Application of "Biomonitor" Species

Current temporal and spatial contaminant monitoring programmes in Ireland primarily focus on the use of biomonitor species, such as bivalve molluscs, to act as a proxy indicator of contaminant levels within the water column. This is because in general, any contaminants accumulated by a biomonitor organism represent the bioavailable fraction present in the sampled medium and many of the pollutants may be highly concentrated in the tissues of such organisms.[18,19] Such tools are widely used and in line with the OSPAR guidelines.

1.1.4.3 Analysis of Sediments

The ultimate fate of POPs in an aquatic environment is linked to sediments. It is generally accepted that the world‘s oceans are the final recipients and the ultimate sink for many contaminants.[20,21] Hence the analysis of sediments can give a valuable insight into the presence of persistent pollutants in aquatic environments. Inland and coastal waters are subject to long term pollution with waste organic matter from human activities. This organic matter can contain a wide variety of anthropogenic pollutants.[22] Once present in the sediment these contaminants can become a base for transfer of chemicals to benthic biota through ingestion or absorption from sediment particles and the water column. Anthropogenic pollutants deposited in this manner can then biomagnify from benthic species throughout the food web.[23] Sediment monitoring must account for critical co-factors that are strongly associated with contaminant concentrations such as grain size and amount of organic carbon.

1.1.4.4 New Tools for Monitoring

ICES and OSPAR are also developing tools for integrated chemical and biological effects monitoring to facilitate more robust assessments of marine pollution status. Such integrated toolsets involving both chemical monitoring of various matrices and biological effects monitoring are regarded as the way forward for monitoring pollution status of the marine environment.[13, 6]

In the absence of reliable instruments for semi-continuous *in situ* measurement of relevant target contaminants in water, passive samplers provide a new approach to monitoring that allows estimation of time-integrated dissolved water concentrations of POPs at levels generally well below those that can be achieved using spot sampling

techniques. Pollutants of interest to this study are briefly described below while a potential role for passive sampling in supporting monitoring and assessment objectives is discussed in greater detail in chapter 2.

1.2 Persistent Organic Pollutants (POPs)

The behaviour and fate of chemicals in the environment is determined by their chemical and physical properties, and also by the nature of their environment. Many organic contaminants are effectively broken down in the environment however some contaminants, as a consequence of their chemical and physical characteristics, are resistant to environmental degradation.[24] The characteristics of a compound are determined by its structure *i.e.* the geometric nature of the atoms present in the structure of the molecule.[25] Depending on the structure of the molecule the physical and chemical properties of these compounds can span a large range of values. It is understood that few substances possess properties, such as persistence and mobility that make them POPs however PAHs, PCBs, OCs and PCDD/Fs have these characteristics and are further discussed in the following sections.

1.2.1 Persistence, Mobility and Bioavailability

POPs may be classified as persistent in the environment if they are reported to have half-lives ($t_{1/2}$) of greater than 6 months *i.e.* the length of time the compound can remain in the environment before being broken down or degraded to a concentration which is half of its original concentration.[26] They must be semi-volatile in that they must have sufficient volatility to evaporate and condense in air, water and soils at environmental

temperatures. Generally these substances are halogenated, have a molecular weight between 200 and 500 g/mol and a vapour pressure lower than 1000 Pa. These properties confer a degree of mobility through the atmosphere which means that POPs can be transported over long ranges from highly industrialised regions to non-industrialised regions.[27]

POPs in general possess high lipophillicity (Log K_{ow} >5), which means POPs can concentrate in the fat and lipid of marine organisms. K_{ow} is defined as the ratio of a compounds concentration in octanol in relation to its concentration in water when the two phases are in equilibrium. Octanol is used in this case as it mimics the solvation properties of lipids and biomembranes. Hence Log K_{ow} can be used as a measure of a compounds lipophilicity or hydrophobicity which can then be associated with its potential bioavalibility. Since the values for organic chemicals can range from 10^{-3} to 10^{7} the values are expressed on a log basis.[27] Because of higher Log K_{ow} values many of these substances have a high bioaccumulation potential.

POPs also have potential toxic or adverse effects on the reproduction, development and immunological functions of aquatic organisms because of the ability to accumulate biologically. Many POPs have also shown endocrine disrupting effects and some are classified as carcinogenic, mutagenic and co-mutagenic.[28] As a result the levels of these substances freely available in the environment should be monitored to protect marine organisms and consequently consumers of marine produce.

There is a wide range of POPs of interest to the environmental scientist however this study will concentrate on OCs, PAHs, PCBs and PCDD/F as they are covered by either national or international legislation or conventions (*e.g.* Directive 2008/105/EC).

Further consideration will also be given to pentachlorophenol (PCP) as it is relevant to the wider scope of this thesis.

1.2.1.1 Bioaccumulation of POPs

Bioaccumulation of POPs by an organism can occur through a variety of mechanisms including bioconcentration, bioaccumulation and biomagnification.[29]

1.2.1.1.1 Bioconcentration

Bioconcentration occurs as a result of direct interaction of an organism present in the sampled media with the freely dissolved concentration of contaminants present. Although the freely dissolved concentration of contaminants, including PAHs present is generally in low abundance (<1 part per billion) [29] organisms can accumulate these contaminants to higher levels in their tissues. Accumulation of contaminants in marine species can occur through aqueous, sedimentary or dietary pathways.[30] The bioconcentration of chemicals from the surrounding environment is dependent on a number of factors including the species, sex, health status, age and growth rate of the organism in question, the physical and chemical properties and bioavailability of the contaminant and the condition of the sampled media with respect to flow rates and temperature.[27] Passive sampling techniques have an especially relevant role in this context.

1.2.1.1.2 Bioavailability

The accumulation of contaminants in marine organisms is dependent on the concentration of POPs dissolved in the water mass at the interface between the organism and the environment.[31] Many processes including: adsorption to sediments and other water bound materials and macromolecules, binding to particulates and

dissolved matter and formation of colloidal suspensions can all reduce the bioavailability of hydrophobic chemicals.[27]

1.2.1.1.3 Organism Status in Bioconcentration

The uptake of POPs from the surrounding environment by marine organisms is generally considered to be a partitioning process between the lipid of the species and the surrounding media.[32] In general the greater the lipid content present in the tissues of an organism the greater the potential for bioconcentration.[33] Under normal conditions the lipid concentration will increase with a higher body weight as the organism ages, facilitating a greater potential for bioconcentration. However many aquatic species may lose lipid during spawning, or have a lower lipid content due to stress, poor feeding grounds or the toxic effects of the chemicals sequestered by the organism. Hence these factors must be taken into consideration when using monitor organisms to model contaminant profiles in the aquatic environment.[19]

1.2.1.1.4 Affect of Physico-Chemical Properties

Bioconcentration in aquatic organisms is dependent on the physical and chemical properties of the media such as pH, or temperature and on the properties of contaminants including lipophilicity and molecular weight. For example Geyer *et al.* [27] established a quantitative link between lipophilicity of the chemicals and the degree of bioaccumulation in an organism (Alga *chlorella fusca*). In general the higher the Log K_{ow} value of a non-metabolised chemical, the greater the potential for bioconcentration in an aquatic organism.[27, 34]

1.2.1.2 Bioaccumulation

Bioaccumulation, as opposed to bioconcentration, can be described as the uptake and retention of bioavailable POPs from any source including water sources, intake of food and contamination from air.[35] Bioaccumulation occurs when the uptake rate of a chemical in an organism is greater than the ability of the organism to metabolise or eliminate the chemical.[36] Bioavailable chemicals whose physical and chemical properties facilitate bioaccumulation will accumulate through any pathway available (usually dietary or passively through contact with surrounding medium) until the chemical concentration in the tissues of the organism reaches equilibrium with the surrounding environment.[37]

1.2.1.3 Biomagnification

Biomagnification of POPs throughout a food chain takes place when apex organisms consume the lower food chain animals. Hence chemicals, which may be in relatively low abundance in the lower food chain animals, can be biomagnified to a much higher level in the apex food chain animals. This process is often referred to as trophic transfer.[31]

1.3 Polyaromatic Hydrocarbons (PAHs)

PAHs are ubiquitous chemical pollutants that are introduced into the environment from a number of different sources. PAHs consist of molecules containing fused benzene rings, where fusion is considered as a sharing of a pair of atoms.[26, 38] The resulting geometric structure is one in which all the carbon and hydrogen atoms lie in one plane. The lowest PAH in terms of amount of fused rings present in its structure and thus molecular weight is naphthalene (C_{10} H_8) with the highest being coronene (C_{24} H_{12}).

In this range there are a large number of PAHs differing in the number and position of aromatic rings with varying physical and chemical properties. These properties vary approximately in a regular trend with molecular weight thus PAHs differ in their environmental behaviour and interactions with biological systems. PAHs originate from both natural and anthropogenic sources and are generally distributed in plant and animal tissues, surface waters, sediments, soils and air. Although they are not acutely toxic to most forms of life several PAHs are suspected or known carcinogens, mutagens, and co-mutagens.[38] The addition of alkyl substituents can enhance the carcinogenic potency of PAHs whereas hydrogenation and methylation can cause a decrease in potency. Halogenation, generally in industrial processes, can greatly enhance their persistence and toxicity in surface waters.[38]

As PAHs are persistent and bioaccumulative, they have been recognised as requiring priority action by OSPAR since 1994 and as such are included in the 1998 OSPAR [9] list of chemicals for priority action. PAHs are also included in Directive 2008/105/EC on environmental quality standards (including naphthalene) as part of the WFD. [5]

1.3.1 Sources, Uses and Discharge of PAHs

The two main contributors to the formation of PAHs in the environment are the burning of fossil fuels, mainly crude oil and by the incomplete combustion of organic matter.[20] In general PAHs come from two main sources:

1. Petrogenic, including fossil fuels mainly crude oils, bituminous deposits and petroleum products, [44,21]

2. Pyrolytic/pyrogenic, including those formed in natural combustion processes, mainly forest fires and volcanic eruptions, by the combustion of fossil fuels, coal and peat, from the incineration of agricultural, industrial and municipal wastes, from power stations and motor vehicles.

Other sources include wood treatment, chemical industries including the aluminium industry and even cigarette smoke.[21, 39, 40] Although many PAHs have been identified, only a few are produced commercially including simpler PAHs such as naphthalene (manufacture of chemicals such as solvents, lubricants and dyes), acenaphthene (dyestuff) and phenanthrene (intermediates).[26] Thus the combustion of fossils fuels is among the main sources of PAHs in the environment. It should also be noted that a number of PAHs can be produced by biogenic processes, for example perylene, however this is not a significant source.[26]

It is possible to distinguish between both petrogenic and pyrogenic sources by studying a variety of concentration ratios.[41] Lower temperature generation of PAH yields abundant alkyl-substituted compounds and thermodynamically favoured isomers as found for petrogenic sources where as high temperature processes (pyrolytic sources) generate mainly parent compounds. This ability to identify PAH sources is further discussed in section 1.3.3.

1.3.2 Pathways of Distribution

There are numerous sources of PAHs in surface water including municipal and industrial effluent, atmospheric (depositions of airborne particulates and precipitation) and aquatic (*e.g.* road run off, sewage spills and oil spills) pathways. In the case of

atmospheric deposition combustion of coal and forest fires are the most important sources of PAHs (*i.e.* pryogenic sources).[26] From combustion sources, under oxygen deficient conditions, PAHs are emitted to the air, usually attached to particulate matter, where no abatement systems are in place. Once they have reached the marine environment PAHs can be grouped into two classes:

1. Lower molecular weight 2 – 3 ring compounds which are volatile and relatively toxic to aquatic organisms.
2. Higher molecular weight compounds with 4 – 6 rings which are not acutely toxic but have been proven to be carcinogenic.

Although PAHs are only slightly soluble in water owing to their high molecular weight and low polarity, they are sorbed by particulate matter on entry to water and thus are deposited in sediments usually in high concentrations. Marine aquatic water in general contains low PAH concentrations, however the aquatic organisms present in the water body can have concentrations several orders of magnitude higher than the surrounding media.[26] Once present in the marine environment the lower molecular weight PAHs are depleted through volatilisation, microbial oxidation and sedimentation where as the higher molecular weight compounds are removed by photooxidation and sedimentation.

Volatilisation can be a significant transport process for 2-ring PAHs *e.g.* naphthalene. Lee *et al.* [42] showed that up to 50% of the naphthalene contained in a marine oil spill was lost depending on various environmental parameters including water temperature and wind speed. The evaporation rate of PAHs also decreases with decreasing vapour pressure. The rate of change is inversely related to the number of aromatic rings hence

higher molecular weight compounds will have insignificant losses due to volatilisation.[43]

Photolysis on the other hand occurs in the presence of atmospheric oxidants or sulphur oxides and can convert PAHs into other compounds some of which can be carcinogenic *e.g.* quinones.[26] Under ozone and light the half lives ($t_{1/2}$) of PAHs can vary from a few minutes to hours.[44] Alkyl PAHs appear more susceptible to photodegradation than the parent PAHs. The products of the interaction of PAHs with oxygen and light are usually endoperoxides, which can undergo secondary reactions to yield a variety of products, including diones. PAHs sorbed to particulate matter are more susceptible to photooxidation however the rate of oxidation will decrease with increasing depth due to a reduction of solar radiation and temperature at depth in a water body. Thus photooxidation of PAHs will be negligible in sediments.

In the case of biotransformation, microorganisms present in the soil, sewage or sea water are capable of degrading PAHs.[26] Lower molecular weight PAHs *e.g.* naphthalene, can be completely degraded to H_2O and CO_2 by the bacterium *Pseudomonas putida*.[45] Higher molecular weight compounds can form phenolic and acidic metabolites. Further transformation can occur once these metabolites enter aquatic animals and the food chain including the formation of intermediates which are known or suspected carcinogens.[26]

1.3.3 Identification of Environmental PAHs

As previously mentioned PAHs have different distribution patterns according to their pollution sources. Isomer ratios such as phenanthrene/anthracene (P/A) and the

flouranthene/pyrene (Fl/Py) ratio can help identify pyrogenic sources while comparison of alkylated PAHs with their parent compounds, an example using methylphenanthrene/phenthene (MP/P) and (Fl + Py/MFl + MPy) flouranthene+pyrene/methylflouranthene+methylpyrene indices can give an indication of petrogenic contamination (*Table 1.1*). Also used in the determination of the source of environmental PAH contamination is the comparison of the sum (concentration) of low molecular weight PAH compounds (three rings or less) divided by the sum of high molecular weight PAH (four to six rings) compounds. A high ratio (>1) can indicate that PAHs with a petrogenic source may be present where a low ratio (<1) can indicate a pyroyltic origin.[46]

Table 1.1 Typical PAH concentration ratios for pyrolytic and petrogenic origins reproduced from Webster *et al.*[20]

Origin	P/A	Fl/Py	Mp/P	Fl + Py/MFl +MPy
Pyrolytic	<10	>1	<1	~3
Petrogenic	>10	<1	>1	<3

Phenanthrene/anthracene (P/A) and the flouranthene/pyrene (Fl/Py) ratios are indicative of the source of PAHs as phenanthrene and pyrene are more thermodynamically stable than anthracene and flouranthene, resulting in a higher proportion of these compounds if the source is petrogenic.[47] The P/A ratio is temperature dependent and decreases with increasing temperature thus high temperature processes can be characterised in low P/A values (<10). The slow thermal maturation of organic matter in petroleum is governed by thermodynamic properties and leads to a much higher P/A value (>10).[20] It must be noted however that high P/A ratios can also be found in sediments from remote areas as a result of photooxidation of anthracene during its long range atmospheric transportation and therefore the P/A ratio is a less reliable source input indicator.[22]

Similarly, the flouranthene/pyrene (Fl/Py) ratio is often used to distinguish between pyrogenic and petrogenic sources with values of >1 being associated with pyrogenic sources.[20] The comparison of alkylated PAHs with the parent compound, using the MP/P and Fl + Py/MFl + MPy indices can be used to identify petrogenic origins in that alkylated homologues are deficient in combustion generated PAHs, giving an MP/P ratio of <1. Fl + Py/MFl + MPy values of near three have been found in sediments where the main source of contamination is pyrolysis with lower values indicating a smaller pyrogenic and greater petrogenic input.[20,47]

By plotting the Fl/Py ratio against either the MP/P or the P/A ratio a petrogenic or pyrogenic zone can be identified (see *Fig 1.1*).[48] The zones defined by high Fl/Py ratio and low MP/P or P/A are identified as pyrogenic where a low Fl/Py ratio and a high P/A or MP/P ratio are characteristic of petrogenic sources. Plotted ratios which fall in the other two quadrants may indicate a mixed source of PAHs.[47]

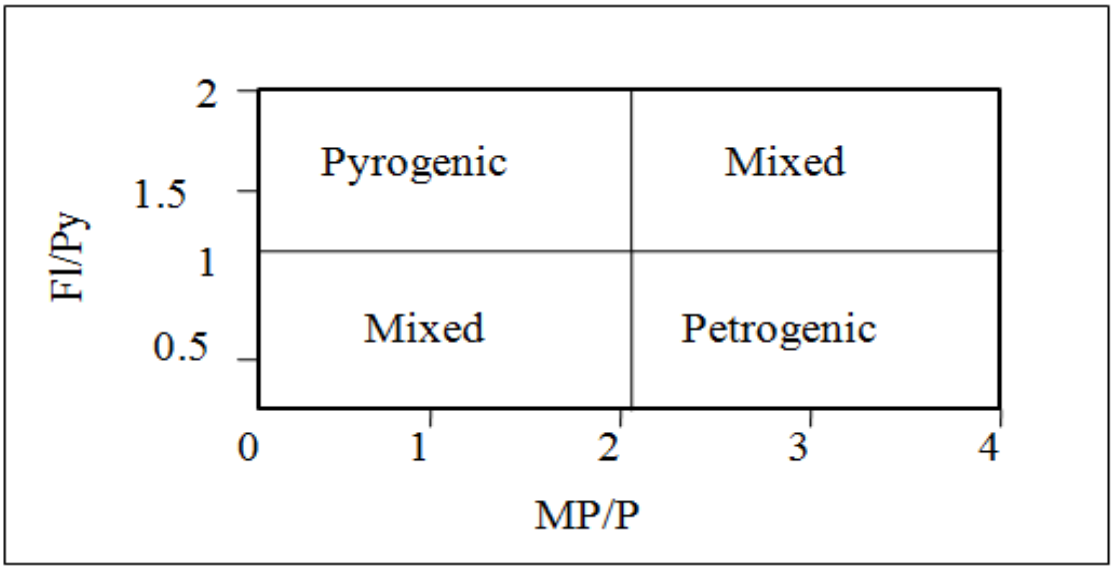


Figure 1.1 Source of identification plot of flouranthene/ pyrene (Fl/Py) ratio against methylphenanthrene.

1.3.4 Structure and nomenclature

PAHs are composed of fused aromatic rings which results in a molecule where all atoms (carbon and hydrogen) lie in one plane. Several systems of nomenclature have been used to describe PAHs with the IUPAC system being the most widely accepted.

PAHs may contain five, six or even seven ringed systems although compounds with six rings or less are the most intensely studied. Compounds of this type (3-6 ring systems) are often targeted for environmental measurement and are listed on the US-EPAs priority pollutant list. Several PAHs exist as alkyl homologues, with the parent nonalkylated compound (C0) and monoalkylated (C1), dialkylated (C2), trialkylated (C3) and tetraalkylated (C4) compounds.[47] The relative abundance of these homologues being indicative of the source of PAHs and the degree of weathering, for example highly weathered oils often exhibit the profile C0<C1<C2<C3<C4. Hundreds of PAHs have been identified with sixteen of these PAH analogues being most often studied as a result of their volatility. Sixteen PAHs are contained in the US EPA list of priority pollutants and are shown, with their chemical structures, below in *Fig 1.2*.[49]

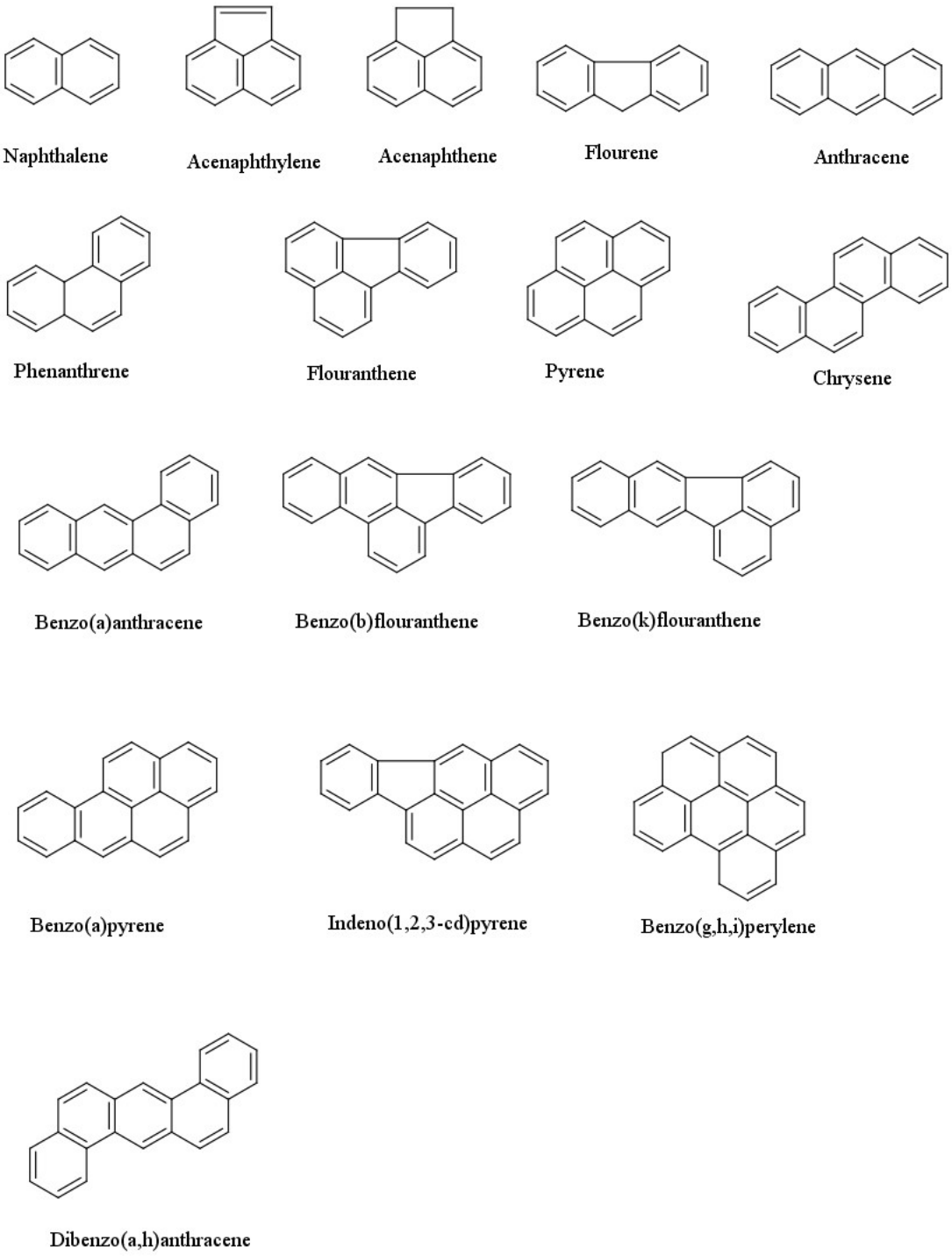


Figure 1.2 The chemical structure of the 16 US EPA priority PAHs (Graphic reproduced from Anyakora *et al.)* [49]

1.3.5 Properties of PAHs

The physical and chemical characteristics of PAHs vary with molecular weight, low molecular weight compounds can be directly toxic to marine animals where as metabolites of some of the higher weight molecular compounds are potent animal and consequently human carcinogens.[50] PAH resistance to oxidation, reduction and vaporisation increases with increasing molecular weight, where as the aqueous solubility of these compounds decreases.[38] PAHs can be divided into two classes based on their chemical and physical characteristics. The lower molecular weight compounds (2 – 3 rings) generally exhibit little or no carcinogenic activity but are acutely toxic where as some of the higher molecular weight compounds (4 – 6 rings) are known to be mutagenic and carcinogenic.[39] *Table 1.2* below shows the various chemical and physical characteristics of PAHs.

Table 1.2 Physical and chemical properties of PAHs

PAH (Symbol)	Molecular Weight	Cas Number	Chemical Formula	No. of Rings	Log K_{ow}	Melting Point (^{o}C)	Boiling Point (^{o}C)
Naphthalene (N)	128.2	91-20-3	$C_{10}H_8$	2A	3.35	80	217
Acenaphthylene (Acy)	152.2	208-96-8	$C_{12}H_8$	2A1C	3.61	92	265
Acenaphthene (Ace)	153.2	83-32-9	$C_{12}H_8$	2A1C	3.92	95	96.2
Fluorene (F)	166.2	86-73-7	$C_{13}H_{10}$	2A1C	4.18	116	295
Phenanthrene (P)	178.2	85-01-8	$C_{14}H_{10}$	3A	4.52	100	340
Anthracene (A)	178.2	120-12-7	$C_{14}H_{10}$	3A	4.50	218	342
Fluoranthene (Fl)	202.3	206-44-0	$C_{16}H_{10}$	3A1C	5.20	11	375
Pyrene (Py)	202.3	129-0-00	$C_{16}H_{10}$	4A	5.00	156	393
Chrysene (C)	228.3	218-01-09	$C_{18}H_{12}$	4A	5.91	255	448
Benzo(a)anthracene (BaA)	228.2	56-55-3	$C_{18}H_{12}$	4A	5.86	159	400
Benzo(b)fluoranthene (BbF)	252.3	205-99-2	$C_{20}H_{12}$	4A1C	5.78	168	481
Benzo(k)fluoranthene (BkB)	252.3	207-08-09	$C_{20}H_{12}$	4A1C	6.11	215	480
Benzo(a)pyrene (BaP)	252.3	50-32-8	$C_{20}H_{12}$	5A	6.35	179	311
Indeno(1,2,3-c,d)pyrene (IP)	276.0	193-39-2	$C_{22}H_{14}$	5A1C	7.66	163	530
Benzo(g,h,i)pyrene (BghiP)	278.3	191-24-2	$C_{22}H_{12}$	5A1C	6.90	273	550
Dibenzo(a,h)anthracene (DahA)	276.4	53-70-3	$C_{22}H_{14}$	5A	6.75	262	524

Reproduced from the US toxicological profile of polyaromatic hydrocarbons.[51]

1.3.6 Bioaccumulation of PAHs

Bioaccumulation of pollutants by an organism can occur through a variety of mechanisms including bioconcentration, bioaccumulation and biomagnification as previously mentioned (section 1.2.1).[29] In humans, exposure to PAHs arises mainly from aquatic routes, atmospheric routes and through consuming contaminated food products. The varying physical and chemical properties of individual PAHs are reported to have an effect on PAH carcinogenicity. Some compounds have been found to be both carcinogenic and mutagenic *e.g.* benzo(a)pyrene and dibenzo(a,h)anthracene, hence some of their alkylated metabolites have the potential to be toxic. Since PAH contamination rarely consists of a single PAH compound it is generally thought that a toxic equivalency factor (TEF) approach, where individual compounds are assessed for xenobiotic activity, can be used to express the toxicity of complex mixtures.[52]

1.4 Polychlorinated biphenyls

Polychlorinated biphenyls (PCBs) comprise a group of anthropogenic manufactured compounds of 209 individual molecules or congeners, which were commercially produced for a number of applications including as dielectric fluids for capacitors and transformers.[53] The main structure consists of a number of chlorine molecules attached to a biphenyl structure as shown below in *fig 1.3.*

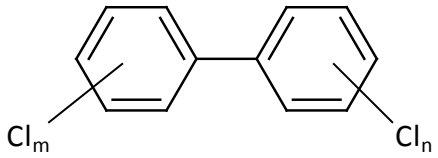


Figure 1.3 PCB general structure comprising a number of chlorine atoms and a biphenyl structure (reproduced from Robertson *et al.*)[53].

Most PCB congeners are odourless, colourless crystals which are soluble in most organic solvents as well as fats and oils.[53] PCBs have low water solubility and low vapour pressures and do not easily degrade under environmental conditions, they also tend to bioaccumulate in animal tissues making them undesirable environmental pollutants.[53] They have been under close scrutiny with regards to their environmental impact for decades and despite an effective ban on their production since the 1970s they remain the focus of environmental attention to this day.[53]

1.4.1 Sources, Uses and Discharges of PCBs

PCBs were primarily commercially produced as complex mixtures containing multiple isomers with differing degrees of chlorination for a variety of applications including as heat transfer fluids, hydraulic fluids, lubricating and cutting oils as well as additives in

pesticides, paints carbonless copy paper, adhesives, sealants, plastics and as dielectric fluids which were used in capacitors and transformers.[53] The Monsanto Corporation, which was the major producer of PCBs and PCB mixtures, marketed these compounds under the trade name Aroclor from 1930 to 1977 where PCBs entered the environment through use and disposal of the contaminants.[27] Poor disposal of fluids containing PCB compounds from transformers and hydraulic fluids as well as capacitors and lubrication/cutting oils are primarily responsible for their introduction into the environment. The volatile nature of PCBs results in atmospheric emissions of PCBs from landfills, spills and road oils. The atmospheric route is recognised as the primary route by which PCBs enter the environment and once present PCBs can remain, resistant to degradation for many years.[53] PCBs can then bioaccumulate in plants and animals and throughout the food chain. PCBs are now considered as ubiquitous environmental pollutants having been reported in nearly all marine and terrestrial biota globally.[53]

Overall levels of PCBs in the environment have been dropping due to the world wide control of disposal practices and the virtual elimination of production, however the ocean provides a sink for these compounds meaning they can still affect marine animal and consequently human health for decades to come.[53]

1.4.2 PCB Structure and Nomenclature

PCBs comprise 209 individual congeners having the basic formula $C_{12}H_{10-n}Cl_n$ where n is the number of chlorine molecules present in the structure. When PCBs are divided by the degree of chlorination *e.g.* trichlorobiphenyl, the term *homolog* is used. The

positions of the chlorine substituents on either phenyl ring are then denoted by numbers assigned to each carbon in the ring (See *Fig 1.4* below).

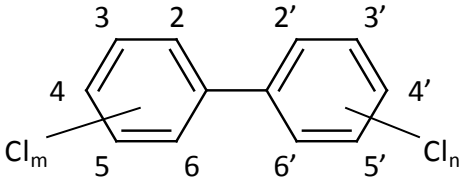


Figure 1.4 PCB structure with numbers indicating the positions of possible chlorination. (m and n indicate the number of chlorines present on each ring)

The position of the chlorine atom in relation to the single bond linking the two phenyl ring structures indicates the position of the chlorine (*meta*, *ortho* or *para* positions). Rotation of the rings can also occur depending on the position of the chlorine atoms which can result in a planar structure or a structure where one phenyl group is at a 90^{o} angle to the other phenyl ring. Many researchers have found the full chemical name (IUPAC) unwieldy and have adopted a number of shorthand nomenclatures including the Ballschmiter and Zell system where the 209 PCB congeners are arranged in ascending numeric order and assigned a number accordingly.[54] Using this system the PCB compound described using the IUPAC system as 2-chlorobiphenyl is described as PCB 1 and the compound described using the IUPAC system as decachlorobiphenyl is PCB 209 with all other congeners in between.[54] This system is widely used internationally and will be utilised in this thesis.

1.4.3 Properties of PCBs

Commercially available PCBs were sold as a complex mixture with a large number of different congeners present. Most PCB congeners are odourless, colourless crystals with low water solubility and vapour pressure and are very stable compounds.[26,53] The degree of chlorination (19 -71 %) is important in understanding their physical and chemical properties as congeners with low percentage chlorination are more soluble and volatile than those congeners with a higher percentage chlorination.[53]

The characteristic of most importance regarding bioaccumulation is the Log K_{ow} value for PCBs which is indicative of a hydrophobic and lipophilic nature. As a result PCBs tend to favour a non-polar phase and will partition away from water to most solids and in the marine environment this includes suspended particulate matter. Some PCBs have been identified as dioxin like compounds because of the spatial orientation of their chlorine atoms on the biphenyl ring and these PCBs (12) have relative toxicities 100 – 1000 times greater than other PCB congeners. In this case they have been assigned TEF factors relative to 2,3,7,8-tetrachlorodi-*p*-dioxin (TCDD) which is the most toxic.[53]

1.4.4 Bioaccumulation of PCBs

Since PCBs are lipohpilic in nature they accumulate in the lipids of animals, including marine organisms, hence they can accumulate in food chains so it is assumed that the population receives the majority of PCB exposure from food intake.[27,53] Because PCBs accumulate in the lipid of marine wildlife it can be inferred that organisms with a high lipid content can accumulate more PCBs from the environment. Intake of fatty fish from contaminated waters in particular can increase intake of PCBs in humans. It is important to prevent human exposure to contaminated aquatic foodstuffs hence the

bioaccumulation of POPs by marine organisms is of primary importance to the environmental scientist.

1.4.5 Human Health

The major intake and exposure of PCBs to the human population is estimated to be as a result of direct food intake.[55,53] Intake from fatty fish found in contaminated waters *e.g.* the great lakes in North America and the Baltic Sea in Europe, increases the risk in humans of accumulating PCBs.[26] Accumulation of PCBs can cause a wide range of pathological symptoms in the liver of experimental animals, including adenofibrosis and the development of carcinomas.[26] The European Food Safety Authority (EFSA) concluded than no health based guidance is required for non-dioxin like PCBs as the exposure to dioxin like PCBs occurs simultaneously.[56] Hence PCBs have been measured as a total burden incorporating all dioxin and non dioxin like compounds.[53]

There have been a number of major environmental contamination episodes involving PCBs such as the Yusho incident in Japan which was a mass food poisoning incident caused by the ingestion of the indigenous population of a brand of rice oil which was subsequently found to have been contaminated by PCBs. A release of PCBs discharges from two General Electric capacitor plants lead to PCB contamination of portions of the Hudson River in the USA.[53]

1.5 Organochlorine compounds (OCs)

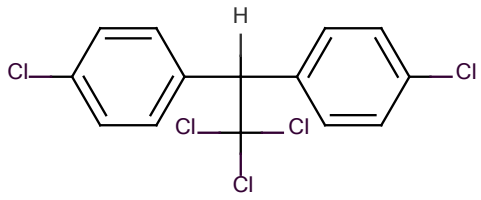


Figure 1.5 Structure of dichlorodiphenyltrichloroethane (DDT) which is the most recognised of all the OC compounds (reproduced from Hester *et al.*) [24]

OCs comprise a small group of anthropogenic compounds characterised by a cyclic structure and a varying degree of chlorination,[26] primarily manufactured since the 1930's and 1940's as pesticides which were subsequently released to the environment, mainly during agricultural processes.[24] During the 1960's public attention was focused on the potentially damaging aspect of the distribution and use of OCs on the environment with the release of Rachel Carson's book entitled '*silent spring*'.[57] Carson highlighted the potential of these compounds for rapid bioaccumulation in the wildlife of affected areas along with the acute toxic effects associated with bioaccumulation throughout various food webs. Subsequently many of the OCs in use were found to present an unacceptable risk to animal and human health in the wider environment. The persistence, mobility and long range distribution potential of OCs has given rise to their presence in the most remote areas of the planet. In 1978 the European council released a framework for the control of the manufacture and use of OCs, [58] however they remain present in the wider environment at low levels.

1.5.1 Sources, Uses and Discharges of OCs

OCs were first synthesised in the 1930's with the use of 2,4-D, which was a phenoxy chlorinated pesticide, followed by hexachlorobenzene (HCB) which was found to be a more environmentally persistent molecule.[24] The similar insecticide hexachlorhexane (HCH) was also released at this time, followed by DDT which was used to control malaria and typhus. The end of World War II provided fresh impetus for the use of improved agricultural methods to provide larger yields.[24] This included the use of a vast array of newer pesticides such as heptachlor and its isomers along with chlordane and toxaphene mixtures. Endrin was marketed in the USA in 1951 followed by endosulphan and its isomers. In the late 1960's once DDT had been banned Mirex was released onto the market to control fire ants in the US.[26] Since then other compounds have been introduced as herbicides and pesticides, however these compounds are characterised by a lower level of resistance to environmental degradation resulting in lower residual levels in the environment.[26]

Once released into the environment as a pesticide, mainly through spraying and dusting of crops, OCs will partition between environmental media according to their physical and chemical properties.[26] OCs can migrate as a result of their semi-volatility, while their low water solubility and high lipophilicity gives rise to preferential accumulation in the fatty tissue of terrestrial and marine animals.[29] Long range distribution of OCs occurs as a result of atmospheric transport which has lead OCs to have a reputation as ubiquitous environmental pollutants.[59,24,60]

1.5.2 Properties of OCs

OCs in general are volatile compounds with low vapour pressures which can allow for vaporisation to air once applied to a crop, particularly if crop dusting is employed as the dispersal method of choice.[24] OCs are classed as persistent pollutants and can travel vast distances through aerial routes. Chemically OCs exhibit high Log K_{ow} values indicating low water solubility and are not found in high levels in the water column.[26] OCs are sorbed to suspended particulate matter in water and the ultimate sink is sediment. OCs are also sorbed by aquatic plants rapidly and efficiently.[24]

1.5.3 Structure and nomenclature

The term OC refers to a group of compounds associated loosely with each other by their common chlorination and by their common uses as herbicides and pesticides. These compounds include several families of isomers including 'the drins' or chlorocyclodiens, which includes compounds with commercially held names such as aldrin, endrin, isodrin and dieldrin.[24] Also included are the hexachlorohexane isomers (γ-HCH, β-HCH and ά-HCH), the chlordane isomers (*cis*-chlordane and *trans*-chlordane) and the isomers of DDT which includes various *meta*- and *para*-chlorinated versions of DDD and DDE. As a result of the large number of 'families' of compounds, as well as their differing structures, a brief guide to structure and nomenclature would prove impossible. OCs are widely discussed in the literature and their chemical structures are well known, hence it would be superfluous to add such a lengthy section here.[24]

1.5.4 Bioaccumulation of OCs

The partitioning of OCs from the environment into biological material, followed by subsequent bioaccumulation throughout food webs is perhaps the most significant aspect of contamination by organochlorine pesticides. Two major routes have been identified for OC contamination, firstly direct vapour phase adsorption to vegetation allows any animal feeding to accumulate contaminants. [61] Secondly if the pesticide has been washed off during precipitation it is subsequently bound to suspend organic matter where it can be ingested by marine animals.[62] Once OCs have been sequestered into the lipid of animals they can accumulate primarily in the animal and subsequently throughout the food chain.

1.5.5 Human health

A list of OCs which are known suspected carcinogens includes aldrin, dieldrin, chlordane, DDT, DDE, heptachlor, lindane and toxaphene and the main areas affected by OC accumulation include the liver, thyroid and adrenal cortex.[26] Apart from carcinogenic properties OCs have also been implicated in cardiovascular disease, hypertension and possibly diabetes. Several pesticides including DDT and DDE have also shown teratogenic affects in laboratory animals though there is no well documented human case.[27] Many studies have found a decrease in the levels of OCs found in humans. A Dutch study on the adipose tissue of humans from 1968 – 1986 found a drop in the levels of DDT from 1.5 to 0.2 μg g^{-1} however the more stable DDE showed no such abatement with levels found from 2 – 3 μg g^{-1}. The decreasing ratio of DDT as regards DDE reflects the greater stability of DDE but also the restriction placed on DDT and hence environmental levels in the developed world.[63]

1.6 Polychlorinated dibenzo-*p*-dioxins

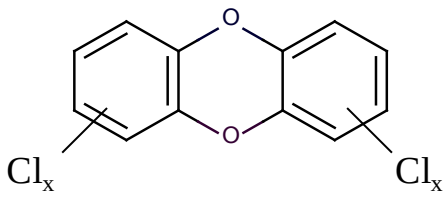


Figure 1.6 Structure of a dioxin molecule, x represents the number of chlorine molecules found in the individual structure (reproduced from Geyer *et al.*)[27].

Polychlorinated dibenzo-*p*-dioxins (PCDD) consist of a group of 75 homologs and isomers which are characterised by being stable, toxic and widespread in the environment. Increasing the halogen content across the two rings has been found to increase the resistance of PCDDs to environmental degradation.[26] PCDDs have attracted considerable concern in recent decades due to their potential adverse affects on wildlife and in humans. It is widely accepted that dioxins have never been directly manufactured but that their sources and apparent omnipresence in the environment has come about as a direct result of their formation as by-products during a number of anthropogenic activities including from the manufacture of OCs.[64, 27,24] Environmental PCDDs may result as by products of a number of industrial processes including in the formation of 2,4,5-trichlorophenol which is present in a number of herbicides and pesticides.

1.6.1 Sources Uses and Discharges

Although PCDDs are ubiquitous environmental contaminants they are not manufactured to any great extent but are commonly inadvertently formed during the production of numerous chlorinated herbicides and preservatives, hence total inadvertent production and release to the environment is difficult to calculate.[26] PCDDs are also formed during combustion processes including municipal and hospital waste incinerators, bleached wood pulp and paper mills, motor vehicles, wood combustion, metal processing and treatment plants and as a bi-product in pentachlorophenol production.[24, 26, 65, 66]

1.6.2 Properties of Dioxins

Dioxins possess low vapour pressures and water solubilities along with high Log K_{ow} partition coefficient values of between ~5.8 and 8.2.[24] Chemicals with these physical properties, when combined with a stable structure allowing persistence in the environment, have shown long range transport capabilities combined with the ability to bioaccumulate and can be toxic to animals and humans alike.[27] The lipophilic nature of PCDDs allows them to partition away from the water phase in the marine environment and allows them to attach to suspended particulate matter. Dioxins are toxic in nature particularly 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) which has been shown to be the most toxic.[27, 24]

1.6.3 Structure and Nomenclature

The term dioxin covers a group of 75 polychlorinated dibenzo-*p*-dioxins which have a basic biphenyl ring structure connected through two oxygen bonds as shown in *Figure 1.6* where n and m represents the number of chlorine atoms present in the overall structure. The compound is an aromatic di-ether which can be chlorinated in positions 1 – 4 and 6 - 9 (*Figure 1.6*). The toxicity of the dioxin molecule depends on the degree of chlorination with the compound TCDD being the most toxic. As such 2,3,7,8-TCDD has been used to test the responses elicited by PCDDs and for the determination of their mechanism of action in animals.[24]

1.6.4 Bioaccumulation of Dioxins

Many studies involving experimentation into the metabolism and bioaccumulation of PCDDs involves the TCDD molecule as it has been found to be the most toxic compound in the dioxin family.[24] TCDD shows little potential for breakdown into less toxic forms once ingested, hence it has the ability to promote carcinogenicity, genotoxicity as well as teratogenic affects.[27] In fact based on acute toxicity studies in several species of animals, TCDD has been found to be the most toxic man made chemical known.[27] TCDD and related dioxins have also been found to be toxic to marine animals especially to newly fertilised eggs, newly hatched and young fish. PCDDs once they are released to the environment can accumulate in various environmental compartments.

1.6.5 Human Health

Dioxin contamination in humans generally occurs through ingestion of contaminated materials including marine life.[24] Although contamination can also occur through occupational and accidental exposure.[27] TCDD has been shown to be toxic and carcinogenic causing issues with cardiovascular and liver function.[26] Many of the other dioxin *homologs* have been shown to be significantly less toxic however. Accidental exposure to PCDDs occurred in Seveso, Italy in 1976 when a chemical factory released a toxic cloud containing high levels of TCDD. The residents in the closest proximity suffered chloroacne and impairment of liver function.[67] More recently, in 2008, Ireland was the source of a dioxin scare where oil from a transformer contaminated the feed of pigs resulting in the banning of pork products for a short time.[68,69]

1.7 Pentachlorophenol (PCP)

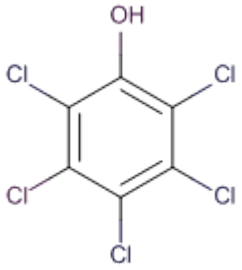


Figure 1.7 The chemical structure of pentachlorophenol (Carvalho *et al.*)[70].

PCP has been dispersed into the environment since the 1930's as a preservative for timber and lumber and is still used today for this purpose among others, including as a pesticide, herbicide and as a molluscicide.[70,71] Due to concerns about PCPs resistance to degradation in the environment and its toxicity it has been recognised as a priority pollutant and its use world wide has been restricted.[70,72,73] PCP residues have been found throughout the environment as a result of extensive past use coupled with renewed usage in developing countries. Although PCP itself is a toxic substance the technical mixture can contain other compounds in trace amounts, as a result of the manufacturing process, which can also be as toxic or even more toxic to man. These can include dioxins and furans as well as hexachlorobenzene (HCB).[74, 71, 75] Despite the fact that PCP has been recognised as toxic and is restricted in many countries (including in Europe) it is a cost effective, available and inexpensive method of treating wood for microbial and insect caused damage.[71] For these reasons it is still used in many countries throughout the developing world.

1.7.1 Sources, Uses and Discharges

PCP is toxic to a variety of microorganisms, plants as well as invertebrate and vertebrate animals and consequently it has been used as a herbicide, pesticide and as a biocide. PCP is primarily manufactured by the chlorination of phenol and by the hydrolysis of HCBs. [71] It has many trade names including 'Dowcide' and 'Pentakil' and besides the use as a pesticide it has also been used as a wood treatment in such products as 'Thompsons Wood-fix' and 'Santophen'. Once used in the environment PCP can evaporate from treated wood into the air and can be broken down as a result of exposure to sunlight.[76] PCP has also been used in the preservation of starches, dextrins and glues, in the construction of boats and buildings and in the treatment of cable coverings, nets and canvas, in paints and in pulp and paper manufacture.[76]

1.7.2 Properties of Pentachlorophenol

PCP has a half life of approximately 2 months in water and 6 months in soil. Its Log K_{ow} values are dependent on the pH but are generally reported at ~5.[76,77] As a result PCP can be accumulated in the lipid compartments of exposed animals and is highly toxic to many marine species at low levels.[72] PCPs breakdown products have been found to be more toxic and resistant than PCP itself causing further concern for its environmental presence.[78]

1.7.3 Bioaccumulation of Pentachlorophenol

In general Log K_{ow} is a good indicator of the bioaccumulation of contaminants. However the concentration of PCP in the marine environment is pH dependent and as the pH affects the Log K_{ow} value of PCP, it is not a good indicator in this case. Values reported for the Log K_{ow} of PCP vary from 1.3 to 5.86. PCP in the environment is therefore not accumulated to a large degree however its breakdown products (pentachloroanisole PClA) and impurities (PCDDs and HCB) can be accumulated readily in the environment making the levels of PCP in the environment important to the environmental scientist.[78]

1.7.4 PCP and Dioxins

The link between the manufacture of PCP and PCDD contamination has been reported frequently in the literature.[68 64, 27, 74, 79] PCP is manufactured by the chlorination and subsequent hydrolysis of HCB or by the direct chlorination of phenol. The impurities found in the technical mixture include PCDD congeners which have characteristic concentration profiles. *Table 1.3* below shows the typical levels of dioxin congeners found from impurities formed during the manufacture of technical PCP. The profile of congeners (*Table 1.3*) shows that the octachlorinated (OCDD) congener is produced in the highest abundance and that the others are produced in less abundance as their level of chlorination decreases.[76] If this fingerprint, or concentration pattern of dioxin congeners is found in the environment it may indicate that the presence of dioxin contamination which can be traced back to technical PCP.[36, 64]

Table 1.3 Total dioxin and furan content formed during the manufacture of technical PCP (reproduced from the IUPAC report on PCP [76])

Compound	Congener (-CDD/F)	Range (ppm)
TCDD	*Tetra-*	0.02 - 1.25
PCDD	*Penta-*	0.03 - 0.08
HCDD	*Hexa-*	0.03 - 38
HpCDD	*Hepta-*	0 - 870
OCDD	*Octa-*	0 - 3300
TCDF	*Tetra-*	0.02 - 0.9
PCDF	*Penta-*	0.03 - 0.65
HCDF	*Hexa-*	0.03 - 39
HpCDF	*Hepta-*	0.1 - 320
OCDF	*Octa-*	0.1 - 300

1.8 Brominated Flame Retardants

Brominate flame retardants (BFRs) are a group of organo-bromide chemicals containing a diphenyl ether ring structure populated by bromine molecules as shown in *Figure 1.8* below.

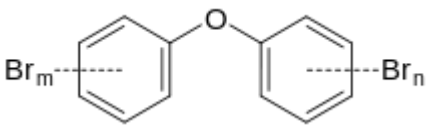


Figure 1.8 Chemical structure of Brominated flame retardants, m and n represent the number of bromine molecules present.

Polybrominated diphenyl ethers (PBDEs) are widely used across industry primarily as an additive in polymers for electrical devices to improve their flame resistant properties.[33] The use of PBDEs has increased in recent times due to stricter fire regulations in many countries.[80]

1.8.1 Sources, Uses and Discharges

PBDEs are commercially produced by the direct bromination of diphenyl ethers in the presence of bromine with a catalyst and these technical mixtures are generally a combination of various congeners which are generally classified into three groups: [27]

1. Low brominated products which are mixtures of tetra-, penta- and hexa brominated diphenyl ethers
2. Octa- brominated diphenyl ethers
3. Deca-brominated diphenyl ethers

Some brominated compounds are additives to polymer mixes and may not be chemically bound hence they can leach or separate from the final product and enter the environment.[81] BFRs can be unintentionally spread in the environment mainly during the manufacturing processes or through incorrect disposal of products containing BFRs. Bio-degradation is thought not to be a main pathway for BFRs to enter the environment but photolysis and pyrolysis studies may be of interest in relation to the fate of these chemicals once in the environment.[82]

1.8.2 Structure and Nomenclature

PBDEs are a family of a possible 209 congeners with the basic chemical formula $C_{12}H_{10-n}Br_n$ where n is the number of bromine molecules present in the structure. As with PCBs, a numbering system analogous to the Ballschmitter and Zell system [54] as discussed in section 1.4.2 is also used for PBDEs.

1.8.3 Physicochemical Properties of BFRs

PBDEs, similarly to other POPs, have low vapour pressure and high Log K_{ow} values (6 – 10) which makes them easily dispersed in the environment where their low water solubility and lipid affinity results in bio-accumulation to any animals in the environment. PBDEs are also persistent in the environment where a half life ($t_{1/2}$) of 600 days has been reported for a penta-BDE in marine sediment by the Scottish fisheries research service (FRS) [83] which is longer than the 50 days it takes to qualify a compound for consideration for the WFD.

1.8.4 Bio-accumulation of BFRs

In 1981 PBDEs were found in fish from Swedish rivers and from various matrices in the Baltic sea.[27] The presence of PBDEs in sperm whale blubber indicates that these compounds have reached the deep sea. PBDEs have also been found in human adipose tissues.[27,84] PBDEs have high Log K_{ow} values and as such are considered to be compounds which can easily accumulate to high amounts in the lipids of animals. PBDEs intake is through ingestion and can magnify throughout food chains.[84]

1.9 Conclusion

It is now widely acknowledged that chemical pollutants can have an adverse impact on the environment and on animal and human health, hence it is vital that these contaminants be monitored on an ongoing basis. Key legislative frameworks and conventions in addition to core parameters have been identified and discussed. Passive sampling technologies are rapidly gaining confidence as a robust method for the sampling and quantitative analysis of a broad suite of environmental contaminants including PCBs, OCs and PAHs. PS has the potential to supply time weighted average concentrations which can take account of spatial and temporal trends as well as any contamination episode that may occur during deployment and thus to supply vital information on levels of POPs in an array of water types which can be used to satisfy Ireland's legislative commitments and to provide information which is important in future planning and management of our marine and freshwater resources. Chapter 2 further discusses current monitoring practices in Ireland, describes passive sampling concepts and discusses the merits for an ongoing role for PSD technologies in support of Irish environmental monitoring goals.

Chapter 2: Passive Samplers - Theory and Application.

2.1 Introduction

The aquatic environment including lakes, rivers, ground water estuaries and coastal zones, is vulnerable to changes induced by human activities. The advent of the WFD which aims to achieve and ensure "good quality status" of all European water bodies by 2015 poses a huge challenge in monitoring activities.[11] While the monitoring methods required are not specified, the widely accepted method of directive compliance focuses on grab or spot water sampling.

In general current international water quality monitoring programmes strongly rely on spot water sampling followed by instrumental analysis to determine water pollutant levels in the aquatic environment.[13] Grab sampling is expensive and labour intensive and it identifies compounds present at a single point in time however despite such disadvantages this technique is widely accepted for international regulatory and legislative monitoring purposes.[13]

Passive sampling devices are a new innovative method for sampling the dissolved contaminant concentration of a wide range of POPs [85,86] and are fast being recognised as cost-effective state of the art pragmatic tools to identify and measure ultra-trace levels of micro-pollutants in water. PS techniques generally enable much greater sensitivity than can be achieved by "traditional" spot-sampling, potentially improving detection capabilities by orders of magnitude.[13] In the wider context the technique is generally applicable to the screening and/or quantification of dissolved pollutant levels for a wide variety of compounds including, non-polar organic substances (*e.g.* PAHs, PCBs & PBDEs), polar compounds (*e.g.* pharmaceuticals and certain pesticides), trace metals, metalloid and radionuclides and organo-metallic compounds (*e.g.* TBT).

Passive sampling devices can be used to monitor organic contaminants in a variety of locations and environmental conditions and depending on the method used may provide measurements suitable for spatial and temporal assessment purposes.[87] Overall PS devices can often account for seasonal changes and point source discharges and can offer a more representative picture of contaminant concentrations in the marine environment.[88]

A wide range of passive sampling devices is now readily available for sampling a diverse range of compounds including organic and inorganic compounds in water.[13] Careful selection and deployment of appropriate sampling devices followed by targeted instrumental analysis can allow for the calculation of dissolved phase, time weighted, trace level water concentrations of a range of environmentally relevant pollutants.[87, 89]

To assess the overall usefulness of passive samplers as a potential monitoring tool for the Irish marine environment a comprehensive literature review was first undertaken. This review concentrated on the various types of passive samplers and their past and potential future use. This pertinent information generated as part of the review is further illustrated in this chapter.

2.1.1 Objectives of Literature Review

The key objectives of this review are to assess the suitability of employing passive sampling devices (PSDs) as chemical monitors by;

- Reviewing current sampling techniques and analysis practices to incorporate the advantages and disadvantages of passive sampling relative to “traditional” spot sampling techniques,
- Reviewing the previous extent of use of passive sampling in Irish waters specifically the levels of POPs and other emerging compounds such as pharmaceuticals and endocrine disrupting compounds,
- Discussing the potential of passive sampling as a “new” monitoring tool,
- Examining the application of passive samplers to measure contaminants relevant for Irish regulatory monitoring purposes;
- Evaluating the potential for wider application of the technique and specifically the potential for incorporation of passive sampling derived concentration data in levels and effects of “integrated” studies.

Chapter 2 does not seek to provide an exhaustive list of emerging or existing techniques in regard to chemical monitors for the marine environment but focuses on discussing advantages and limitations of passive sampling and overall suitability of PS as a monitoring technique. Ultimately this chapter reviews the current state of the art with respect to key passive sampling methodologies incorporating summaries of, and key technical considerations of each, including, quality assurance aspects, availability and use of performance reference compounds to evaluate membrane sampling rates, range

of potential analytes, extraction/analytical methodologies and discusses the suitability and robustness of these devices for extended deployment periods in Irish marine waters.

2.1.2 Practices in Sampling and Analysis

Sampling and analysis of the marine environment requires sensitive analytical methodologies which can allow for the detection of a broad range of persistent pollutants (including PCBs, PAHs, organochlorine compounds and PCDD/Fs) found in marine organisms and the water column itself. Until recently many marine monitoring programmes relied on spot water collection to provide samples for analysis.[13,85] This type of traditional sampling, though problematic, is generally accepted for legislative monitoring however these types of sampling techniques can often present an unrepresentative picture of the environment as considerations such as seasonal variations and point source discharges are generally not taken into account.[90,91]

In order to derive a broader picture of water quality and the potential for deleterious effects, monitoring programmes are best served where an array of integrative sampling techniques and matrices are utilised thus providing a more representative picture of water quality.[86]

The development of environmental passive samplers began in the 1930s but these devices could not be mathematically characterised until the 1970s.[92] Passive samplers which could be used to measure volatile organic compounds in water were first developed by Soedergren in 1987 where a dialysis membrane containing hexane was used to simulate the uptake of pollutants by aquatic organisms.[93] In 1990 Huckins *et al.* [94] described the use of a bi-phasic semipermeable membrane device (SPMD) which was

filled with a synthetic lipid triolein which was also used to sample the marine environment for volatile organic compounds (VOCs). Since then the use of passive sampling devices for monitoring both organic and inorganic species of contaminants has been widely reported.[95]

PSDs can be used for sampling and analysis of a broad range of environmentally persistent pollutants related to this study including PCBs and organochlorine compounds (OC) as well as PAHs.[96,85] Passive samplers can also be used in the study of inorganics and heavy metals as well as a wide range of emerging Endocrine Disrupting Compounds (EDCs).[97,98] A number of passive sampling devices (PSDs) are now recognised to have the capacity to enable time weighted average (TWA) dissolved pollutant levels to be derived, which takes into account seasonal impacts as well as the effects of point source discharges.[88]

This diversity of sampling applications and the potential to give a time weighted average (TWA) concentration which takes into account seasonal variations and point source discharges alike makes the passive sampler an ideal method for marine environmental pollution monitoring especially those focussing on hydrophobic pollutants.[13]

2.2 Passive Samplers: Common Underlying Concepts

General sampling theory, the range of possible analyses, the underlying mechanisms of operation and uptake/accumulation, the use of performance reference compounds (PRCs), PSD suitability for deployment in harsh environmental conditions over medium to long periods and quality assurance aspects of passive sampling are all further discussed below with the aim of determining the overall usefulness of PSDs as environmental monitors. As it is necessary to monitor pollutants in the aquatic environment for surveillance monitoring and to satisfy legislative frameworks and directives, the use of appropriately selected passive samplers can potentially provide an excellent technique to monitor dissolved water concentrations for any number of targeted toxic compounds, including those which have been designated as priority pollutants.[87,86,99]

Passive samplers provide a medium in which contaminants of interest can be retained and sampled accurately. Passive sampling can be defined as any system based on the free flow of analyte molecules from the sampled medium to a receiving phase in the sampling device.[92] Analytes are trapped or retained in a suitable medium within the passive sampler, known as a reference or receiving phase,[30] this phase taking the form of a solvent, chemical reagent or a porous adsorbent.[100]

Passive sampling devices in general possess a barrier between the sampling environment and the receiving phase which determines the rate at which the contaminants can be sequestered at given concentrations as well as providing enhanced selectivity towards different classes of pollutants of interest.[85] Two types of passive sampler are distinguished by barrier type,[95] (i) the diffusion barrier where analyte concentration occurs by diffusion through a static layer of water and analytes are retained once they pass through well defined openings in the samplers and (ii) the

permeation barrier type where accumulation occurs through a porous or non-porous membrane. In general pollutant accumulation from the sampled media to the PSD follows the pattern shown below (*Fig* 2.1).[85,91]

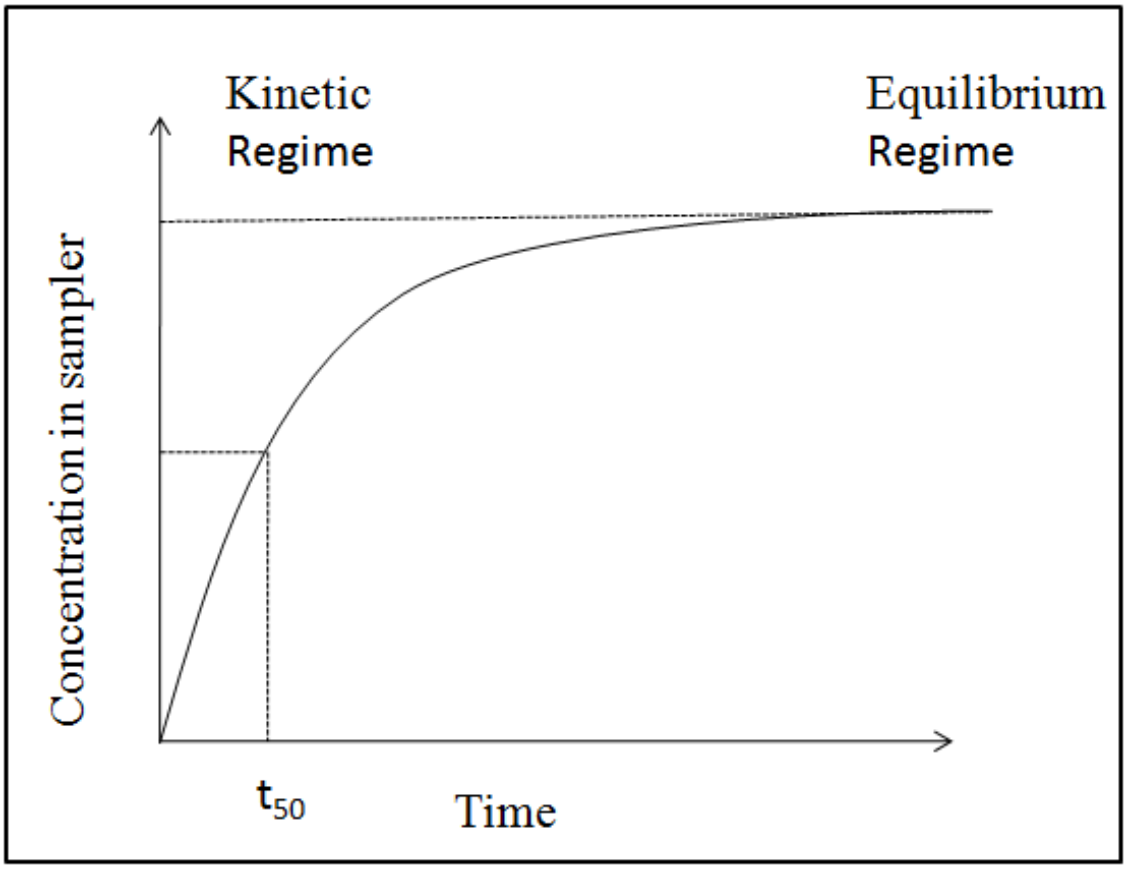


Figure 2.1 The general uptake in contaminant concentration over time for most passive samplers (reproduced from Kot-Wasik *et al.*) [85].

In general, kinetic exchange between the passive sampler and the surrounding water phase can be described as a first order one compartment mathematical model as shown in *Eqn. 2.1*

$$C_s(t) = C_w \frac{k_1}{k_2}(1 - e^{-K_2 t}) \qquad \text{Eqn. 2.1}$$

Where $C_s(t)$ is the concentration of the analyte in the passive sampler at time (t), C_w is the analyte concentration in the aqueous medium and k_1 and k_2 are the uptake and offload rate constants, respectively.

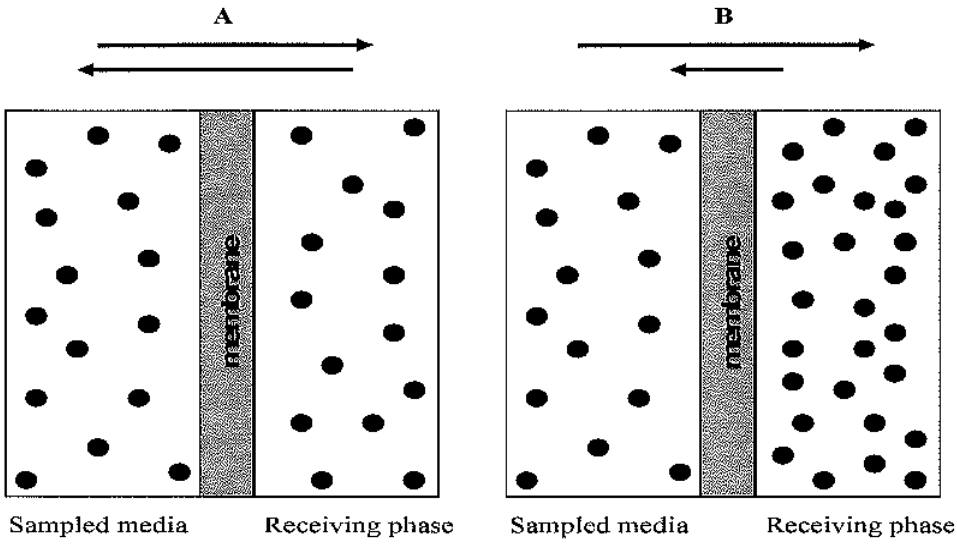


Figure 2.2 Graphical representation of (A) equilibrium and (B) non-equilibrium passive sampling reproduced from Kot-Wasik *et al.* [85]

Figure 2.2 (A) shows the uptake and desorption rates of a sampler which are in equilibrium with the sampled media and only small changes in concentration will occur from then onwards. *Figure 2.2* (B) depicts the sampler in the kinetic or uptake phase where the contaminants are free to move between both phases. The time span required for a sampler to reach equilibrium depends on the capacity of the receiving phase and passive samplers can be characterised as equilibrium and non-equilibrium samplers. These concepts are further discussed below.[13,87,85,95]

2.2.1 Equilibrium Passive Samplers

In equilibrium sampling, the exposure time must be sufficiently long to permit the establishment of a thermodynamic equilibrium between the sampled media and reference phases.[85] In this situation *Eqn.2.1* is reduced to:

$$C_s(t) = C_w \frac{K_1}{K_2} = C_w K_{pw} \qquad \text{Eqn.2.2}$$

Where knowledge of the phase-water partition co-efficient (K_{pw}), or equilibrium partitioning co-efficient allows the estimation of dissolved analyte concentration.[88] Passive samplers operating in this regime require that the sampler capacity is to be kept well below that found in the sampled media to avoid saturation and that the devices response time must be shorter than any fluctuations being measured in the environmental medium. The basic requirements of the equilibrium sampler approach are that stable concentrations of contaminants are reached during a known time period. In the equilibrium sampling regime the equilibrium partitioning co-efficient (K_{pw}) can be used to estimate the concentration of pollutants in the medium by measuring the concentration in the sampler. The more widely used equilibrium passive samplers encompass the devices which are based on solid-phase micro extraction (SPME) such as Passive Diffusion Bag Samplers (PDBSs) which have been used extensively for monitoring volatile organic compounds (VOCs) in water. [101]

2.2.2 Kinetic Passive Samplers

With kinetic or non-equilibrium sampling devices the sampler never reaches equilibrium with the surrounding medium and is constantly in the linear uptake phase within the sampling period.[13] These types of sampler are characterised by a high capacity for collecting contaminants which ensures that the sampler is constantly enriched during the sampling period. With non-equilibrium passive samplers it is assumed that the mass transfer of contaminants from the sampled media to the receiving phase is proportional to the difference between the chemical activity of the contaminant in the sampled media compared to that in the receiving phase.[91] In the initial uptake phase the rate of desorption from the sampler receiving phase to the surrounding media

is considered negligible hence the sampler works in the linear uptake regime and *Eqn. 2.1* is reduced to:

$$C_s(t) = C_w K_1 t \qquad \text{Eqn.2.3}$$

Where the concentration in the sampler (C_s) at time (t) can be used to calculate the concentration in the water phase (C_w) using the upload constant (K_1) per unit time (t). *Eqn.2.3* can be re-arranged to express the amount of analyte accumulated after a given exposure time when the proportionality or sampling rate (R_s) is known:

$$M_s(t) = C_w R_s t \qquad \text{Eqn.2.4}$$

Where $M_s(t)$ is the mass of the analyte accumulated after exposure time (t) and the proportionality constant (R_s) is the product of a first order constant for uptake of a contaminant (k_1) and the volume of water that gives the same chemical activity as the volume in the receiving phase. R_s can be interpreted as the volume of water cleared of analyte per unit of time by the passive sampling device thus the TWA concentration of an analyte in the water phase can be calculated using the formula:

$$C_w = \frac{M_s(t)}{R_s t} \qquad \text{Eqn.2.5}$$

Where M_s is the amount of an analyte accumulated in the sampler after exposure, M_0 is the concentration in the sampler before exposure. Kinetic passive samplers can be used in situations of variable water concentration of analytes and can sequester contaminants from point source discharges and seasonal changes. They can also be used to quantify

ultra-trace level contaminants over extended time periods. For most samplers operating in the kinetic mode the sampling rate (R_s) is not affected by the concentration present in the water phase (C_w) but is affected by water flow and turbulence as well as bio-fouling and temperature.[102] The sampling rate is thus characterised by the individual contaminants of interest under the prevailing environmental conditions during the sampling period and can be estimated using:

$$R_s = k_0 A = k_e K_{pw} V_D \qquad \text{Eqn.2.6}$$

Where k_0 is the overall mass transfer coefficient; A is the surface area of the sampler membrane; V_D is the volume of the receiving phase; k_e is the exchange rate constant and K_{pw} is the receiving phase/water partition coefficient. Since the sampling rate is dependent on the mass transfer coefficient k_0 and the partitioning between the receiving phase and the surface area it is of benefit to have a high sampling rate and high exchange area with low mass transfer resistance.[13]

2.2.3 Modelling Passive Sampler Accumulation in the Environment

Contaminant uptake by passive samplers can be considered as a multi-stage transport process involving molecular diffusion from the water boundary layer (WBL) through a bio-fouling layer, diffusion through a membrane and finally sorption to the central receiving phase.[88] Other stages may cause additional interferences in the uptake rates and may also need to be modelled and these can include the reduction of movement of water where a cage is employed to protect samplers, water turbulence and temperature as well as the physical and chemical properties of the analytes in question.[85,91] A variety of models have been used over the past 15 years to better understand the interactions of

passive samplers with the surrounding environment. These models can differ in the number of phases and simplifying assumptions which are taken into account, such as the existence of steady state conditions or the presence of linear concentration gradients in the membrane phase.[88] Since these variations make a general picture of passive sampling impossible it is therefore worthwhile to apply the various types of modelling to the samplers used and the environmental conditions that are present during the sampling process.

2.2.4 Environmental and Physico-Chemical Factors Influencing Passive Sampling

Although modelling of the multi-stage transport process involved in the transfer of analytes from the surrounding media to passive sampling devices depends on a wide variety of variables there are several environmental factors which affect all passive sampling devices. These can include water turbulence, temperature and the presence of bio-fouling.[13] A number of such factors and techniques to mitigate against these effects are discussed below.

2.2.4.1 The Effect of Water Turbulence on Passive Samplers

Although passive sampling has been widely used and recognised as a valuable environmental analytical tool the reliability of the devices under varying environmental conditions is currently the subject of some controversy.[99] Turbulence of the environmental media is one factor which can affect the uptake rate and thus the final concentration of analytes that may be found in the sampler. Even under laboratory conditions turbulence can be difficult to control thus when sampling in the open environment where no such controls on turbulence are possible modelling of the affects are important.[103] Passive samplers sequester contaminants from an unstirred layer

directly beside the sampler and water turbulence can affect the thickness of the unstirred layer which forms part of the diffusion limiting barrier at the sampler membrane-water surface. As a result of this disturbance of the unstirred layer in dynamic environments the mass transfer rates between the sampled media and the sampler can be affected depending on the type of sampler.[104, 95,13]

Kingston *et al.* [105] describe an experiment in which the analyte concentration and temperature were kept constant with changes in the water turbulence of the system simulated by using differing stirring speeds for two 'chemcatcher' passive samplers using two different membranes (polysulfone and polyethylene). The results indicate that the degree of turbulence has a quantitative affect on the accumulation of analytes by a passive sampling device depending on the diffusion limiting aspect of the membrane chosen and also the physical and chemical properties of the analytes themselves.[105] Hence during field deployment of passive sampling devices changes in water turbulence can be difficult to account for when modelling the accumulation of analytes by PSDs.

2.2.4.2 The Effect of Bio-fouling on Passive Sampler Accumulation

A bio-film can be classified as an amalgamation of microorganisms which can adhere to each other and to any suitable surface. Unprotected surfaces which are submersed in water will eventually become colonised by various flora and fauna which will eventually form a bio-film.[95,106] The thickness of the bio-film can vary from deployment to deployment, between seasons and even at different locations on the sampler membrane. The uptake rates of hydrophobic contaminants in passive sampling devices have been shown to drop with increased fouling.[102,107] The bio-fouling layer can affect the overall resistance to mass transfer by blocking any water filled pores and in essence

acting like an immobilised water layer which adds another compartment to any modelling of uptake rates in the sampler.

Using an approach whereby Performance Reference Compounds (PRCs) are used to model the effect of a bio-fouling layer on the mass transfer of analytes between an aqueous media Booij *et al.* [102] showed that the differences in uptake rates were quantitatively reflected in the dissipation of PRCs – in essence proving that PRCs can be used to correct for any bio-fouling that can take place during the sampling period.[89] The problem of sampler bio-fouling may be improved in some cases with the selection of suitable construction materials and in some cases the addition of a fouling inhibiting solvent from the solvent filled bag type samplers.

2.2.4.3 The Effect of Temperature on Passive Sampling Accumulation

Temperature can play an important role in determining the uptake rate of a passive sampler. From a kinetic point of view it is clear the temperature will have an effect on the mass transfer rates in all media as the temperature can affect the kinetic component of the sampling rate. This effect has also been noted for various sampling devices in various sampled media.[99,86,108] The effects of temperature on passive sampling are not easy to model analytically because of the complexity of the effect on different aspects of the passive sampler system, including affects on the WBL, membrane and on the receiving phase. The different physical and chemical properties of individual analytes may also be affected by temperature. Huckins *et al.* [109] found that the effects of temperature on sampling rate were complex for 15 priority PAHs by sampling with SPMDs, but that the effects were relatively small. Uptake rates for SPMDs were found to increase by a factor of approximately 2 for each 10 ^{o}C increase in temperature on

average.[109] Petty *et al.* [110] found similar results in PAH uptake by SPMDs while Booij *et al.* [111] found higher sampling rates at 30 ^{o}C than at 2 ^{o}C by a factor of about 3.

In the case of PDMS silicone rubber samplers modelled by Smedes *et al.* [89] the sampling rate was found to vary in line with seasonal changes and hence temperature differences in the water column at the sampling site. Smedes found that the sampling rate decreased by 30% with a 10 ^{o}C decrease in temperature which were roughly in agreement for observations made by Booij *et al.*,[111] for silicone rubber samplers, which showed a 100% increase in sampling rate with a 30 ^{o}C increase in temperature.[112]

2.2.4.4 Salting Out Effect of Water

Silicone rubber passive samplers, once placed in the marine environment are affected by the increased ionic strength of the medium. This changes the aqueous solubility and activity of the organic compounds which can in turn affect partitioning and adsorption where PDMS PSDs is concerned. Jonker and Muijs [113] report that the hydrophobicity of organic compounds in salt water is increased which in turn can have an effect on sorption. The effect can be modelled by combining the original Setschenow [114] equation with a liner partitioning equation in effect describing the sorption of compounds between a solid phase (PDMS) and water the following equation is obtained:

$$Log\ K_{pw}^{so} = Log\ K_{pw}^{0} + K_s I \qquad \text{Eqn 2.7}$$

Where $Log\ K_{pw}^{so}$ is the solid phase-water distribution coefficient in salt water (L kg^{-1}) and $Log\ K_{pw}^{0}$ is the solid phase water distribution coefficient in salt-free water. K_s is the salting out - Setschenow constant (L mol^{-1}) and I the ionic strength of the water (mol L^{-1}). Smedes *et al.* [115] report that the ionic strength (I) is approximately linear with salinity

and that the temperature effect on I can be neglected and that the K_s values are constant for the compounds of interest to this study. By using the above equation (*Eqn.2.7*) an estimation can be made of the effect of salting out on sampler-water partition coefficients ($Log\ K_{pw}^{so}$) which is further shown in appendix A.1.

2.3 Performance Reference Compounds

Performance Reference Compounds (PRCs) have been used to compensate for the environmental factors (turbulence, flow rates and bio-fouling) which can affect exchange kinetics during the sampling period.[116,117] The dissipation of PRCs from the sampler to the surrounding medium has been shown to closely follow the uptake of contaminants into the sampler from the environment and so PRCs can be used to predict *in situ* sampling rates.[13,85,87] PRCs are generally labelled or non-labelled non interfering chemical compounds with similar chemical properties to the compounds of interest. Common PRCs for PAHs include deuterated analogues such as naphthalene-d_8 or phenantherene-d_{10} and in the case of PCBs congeners those with the same basic chemical structure which are not found in high abundance in the environment such as PCB 29, 30 or 204.

A range of PRCs (Log K_{ow} 3-7) should be chosen to accurately reflect the range of contaminants which, once spiked to the sampler prior to deployment, should dissipate mimicking the *in situ* uptake kinetics to the sampler during the sampling period.[118] This *in situ* calibration approach is based on theoretical and experimental evidence that the rate of PRC dissipation in to the environment is proportional to the rate of analyte uptake.[116,118] Since the *in situ* sampling rate is critical to the use of passive sampling devices to estimate water sampling rates the use of PRCs can also be used to provide data on the exposure variables encountered by the PSDs during the sampling period.

PRCs may also be used to ascertain which of the analytes of interest have attained equilibrium and which are still in the kinetic uptake phase which is of primary importance in calculating dissolved water concentrations of contaminants.[119] PRC concepts are less developed for POCIS type passive samplers and thus they are generally only utilised for screening purposes rather than derivation of water concentration data.

2.4 Passive sampling: A Review of the State of the Art

In recent times passive sampling has become commonplace in many countries across the EU. Many different types of passive samplers have been developed to sample a variety of contaminants in different environments, hence, the selection of an appropriate passive sampling device capable of measuring the contaminants of interest firstly requires a solid understanding of the modes of action and the advantages and disadvantages of more traditional techniques in relation to the inherent benefits of passive sampling.

2.4.1 Traditional Methodologies versus Passive Sampling Techniques

Sampling has been defined as a process of selecting a portion of material small enough to be transported to the laboratory which would still accurately represent the environment sampled.[13,88] The more traditional sampling methods encompass the grab or spot sampling techniques and currently the most commonly used method is spot (bottle) sampling followed by extraction using solvents and instrumental analysis.[88] This approach is well established and validated and while often problematic it has generally been accepted for international regulatory and legislative water quality monitoring

purposes. Often the main difficulties with traditional methods of sampling are those of sample representativeness and integrity:

- The samples may not be truly representative of the concentrations present as they do not take account of water currents or pollution episodes which may occur;
- As some pollutants are found in very low concentrations, large volumes of water may be needed for analysis;
- For surface water, samples can be collected by filling the sample bottle but for deeper waters this is not as readily possible. Peristaltic pumps or specially designed remotely triggered samplers are needed;
- Spot water samplers reflect water composition only at the moment of sampling and so may fail to spot episodic contamination as well as seasonal and tidal changes;
- Quality control and physical difficulties are often encountered with large volumes of water that must be collected and extracted;
- Concentrations of dissolved contaminants may not be accurately measured by conventional approaches such as spot water sampling.

Current research suggests that a more accurate representative picture of water quality can be obtained by using newer approaches and tools in environmental sampling which can include: [85, 86]

- A higher frequency of spot sampling resulting in a larger volume being sampled and results in lower limits of detection than is possible using conventional sampling methods;
- Automatic sequential sampling which can provide a better picture over time;

- Continuous online monitoring systems;
- Biological early warning systems (such as Mussels and Tubificidae [120]) and passive samplers which can be used to indicate pollution episodes.

Passive samplers mimic biological uptake and can be linked to biological effects based studies.[88,121] Passive sampling techniques can be employed to overcome the shortcomings in traditional sampling methods. In passive sampling analyte concentration is integrated over the sampling time which gives rise to the term time weighted average (TWA) concentrations. These calculations can take into account seasonal variations, point source discharges and spatial trends. Hence Passive samplers are less sensitive to accidental or extreme variations of pollutant concentration. PSD's are not dependent on any power source and can be deployed in many varied and extreme environments. Extraction, clean up of the samplers and instrumental analysis can be a simple procedure with the use of PRC's overcoming any validation issues.[87, 91]

Biological organisms including mussels and oysters as well as newer passive sampling technologies can offer a reliable, robust and cost effective method which can be used for time integrated environmental chemical monitoring programmes.[121]

While PS measures dissolved phase contaminant concentrations and cannot be directly used for WFD compliance assessments (with the exception of metals, WFD EQS are set in total water) they clearly provide an option where EQS cannot be achieved by current analytical methods and provide valuable information to verify compliance monitoring. Passive sampling, in conjunction with sediment and biota sampling, in particular can offer an alternative to the more traditional sampling techniques and has the potential to

become a reliable, robust and cost-effective method which can be used in water monitoring programmes across Europe.[87]

2.4.2 Passive Sampling: A "New" Tool for Monitoring?

The use of infrequent traditional grab sampling of water is ineffective at identifying transient pollution events [85] and cost generally precludes high frequency sampling in coastal waters. More sensitive biological techniques have demonstrated that many compounds have biological effects at trace levels. This has highlighted the importance of developing methods with low detection limits, and has driven the development of more representative sampling methodologies.

The use of passive samplers can provide truly dissolved TWA concentrations in relation to chemical monitoring of the marine environment which can take into account varying hydrological conditions and intermittent pollution episodes and as such PSDs can be a useful supporting technique in a 'toolbox' for monitoring within the WFD and other environmental programs.[13,91]

A number of expert groups of international bodies such as the International Council for the Exploration of the Sea (ICES) and the OSPAR Convention have identified the potential of PS to support marine pollution monitoring programmes such as those required under the Marine Strategy Framework Directive.

Ultimately ongoing successful implementation of the MSFD and/or WFD and other directives will depend on the availability of low cost technologies, such as those identified within the "Screening Methods for Water Data Information in Support of the

Water Framework Directive (SWIFT-WFD)" project [122] and on outputs from initiatives such as the OSPAR/ICES passive sampling study and on continued research into techniques (*i.e* Passive sampling) which will be capable of providing reliable and effective data in support of management goals.[13]

2.4.3 Monitoring of Pollutants: The Current Status

The scope and methodologies currently employed in Ireland in order to comply with national and international water quality legislation and conventions have been detailed in Chapter 1. To date the availability of passive sampling derived analytical data in Irish waters is limited to that of a number of "once-off" research initiatives. The summary details of these initiatives are discussed in the following sections.

2.4.3.1 Passive Sampling Trial Survey (PSTS 2007)

This passive sampling trial survey for hydrophobic organic contaminants in water and sediment and specifically on the use of silicone rubber passive samplers in water and sediment was organised through ICES in response to the decision of OSPAR to support a field trial of passive samplers.[118] Passive sampling materials for water and sediment sampling were prepared by a central laboratory (RIKZ Netherlands) and sent to the participating laboratories where they were exposed to the local marine environment before analysis with replicates being sent to the central laboratory for comparison. Ireland, through the Marine Institute, Dublin Institute of Technology and the Environmental Protection Agency, participated in the PSTS and data was submitted to the ICES coordinating body.[123]

Key objectives of this trial were [118] to transfer knowledge of the methods more widely used within the ICES community and to enable laboratories gain experience in the use, deployment, validation, analysis and in modelling of PDMS passive samplers. Ultimately a convention wide dataset of freely dissolved water concentrations of hydrophobic contaminants in water (and sediment pore waters) across the sampled area was derived. Key conclusions which focussed direction of future PS work included:

- Provision of new information on the distribution of freely dissolved contaminant (PAHs and PCBs) concentration over a wide geographical range which is comparable to the current general understanding of the sources, transport mechanisms, distribution and environmental chemistry of PAHs and PCBs;
- Determination of a strong correlation between bioconcentration factors in mussels and freely dissolved concentrations in water determined by passive sampling validating the use of passive samplers for marine environmental monitoring;
- Data on freely dissolved concentrations found in pore water suggest that PCBs present in the sediment are potentially available to the water phase whereas in the case of PAHs 90% are not available to take part in partitioning with aquatic organisms;
- Passive samplers provide new data on the distribution of freely dissolved contaminants which would not normally be easily obtained.

Irish participation in this initiative comprised of the deployment of silicone rubber passive samplers in tandem with co-deployed transplanted blue mussels (*Mytilus edulis*) as a bio-indicator species, to monitor dissolved water concentrations (C_w) of PCBs and PAHs in Dublin Bay and Galway Bay. PAH and PCB dissolved water concentrations

were found to be generally relatively low in water and mussel samples from both sites, with the most elevated levels observed at the more industrialised Dublin site.[123,124]

2.4.3.2 Novel Passive Sampling Materials for the Screening of Priority Pollutants

The aim of this Dublin City University (DCU) and EPA study was to develop and screen novel passive sampling materials for monitoring priority pollutants such as pesticides and hydrocarbons in the aquatic environment. The polymer films were fabricated from PVC and contained a plasticizer which acted to make the films flexible in nature as well as to enrich the analytes from the water sampled.[125] Measurements were carried out by immersing the polymer films in aqueous solution containing the relevant chemical and the recording an infrared spectra of the exposed material. The results obtained from this small-scale study indicate that there is potential for the materials to be used in the determination of selected priority pollutants in the aquatic environment.

2.4.3.3 Biological effects and Chemical Measurements in Irish Marine Waters

A joint Seachange (MI/EPA funded Project) entitled "Biological effects and chemical measurements in Irish marine waters" utilised passive sampling using Polar Organic Chemical Integrative Samplers (POCIS) devices for the identification of steroidal and non-steroidal compounds and also polydimethylsiloxane (PDMS) strips for the determination of dissolved concentrations of hydrophobic pollutants.[126] POCIS passive samplers were utilised as a valuable screening tool with the naturally occurring steroid oestrogens, oestrone (E1) and 17β estradiol (E2), and 17α ethynylestradiol (EE2) the synthetic oestrogen used in the contraceptive pill was identified but not quantified at a

number of Irish locations. The derived pollutant profiles supported the analytical chemistry in terms of similar pollutant profiles.

Using PDMS PSDs the study reported that the ΣPAH_{15} was elevated in more industrial areas relative to the Omey Is. reference site. PAHs such as phenanthrene, fluoranthene and pyrene predominate in areas with greater marine traffic and general industrial influences. The observed profile in PS devices broadly reflects that for sentinel mussels for the same locations and is predominantly reflective of pyrogenic inputs. HCB and Σ7PCB concentrations were found to be low with all being below respective AA-EQS for these parameters.

Overall these studies have shown that PAH and PCB dissolved water concentrations are generally relatively low in the Irish waters tested, with the most elevated levels observed at the more industrialised areas. It is evident that passive sampling can have a pivotal role in future Irish integrated monitoring programs in support of WFD and MSFD monitoring commitments.

2.5 Selection of Appropriate Passive Samplers

There are many different types of passive sampler which can be used to sample different contaminants in different environments hence the selection of appropriate PSDs is of primary importance to this project. This study continues on from the work of O'Hara [123] and the PSTS 2007 where PDMS passive sampling devices were employed across Europe to monitor POPs, hence the use of PDMS passive samplers in this study. Also used in this study were SPMD passive samplers.

Many data are currently available on the SPMD, which has been in use since 1990.[94] The contaminants of primary importance to this study include PAHs and PCB/OCs which can be broadly classified as being semi-volatile organic compounds (SVOCs) with both PDMS and SPMD devices capable of sequestering these contaminants from the water column.

During the initial planning stages and literature review for this study, consideration was given to other PSDs which may have had the potential to function as devices which could contribute to the fulfilment of Ireland's monitoring requirements. These can include PSDs which can be applied to screen for more polar compounds (POCIS), devices which can be used to screen for metal contamination (Chemcatcher, DGT) and other devices which can sample for POPs (MESCO). Summary information on some commonly used passive samplers (POCIS, Chemcatcher, DGT *etc*) is presented in appendix A.2, however as this current study focuses on both the PDMS and SPMD more detailed mechanisms of operation of these devices are presented elucidating the theoretical use of both type of passive sampling device. In the following sections these PSDs are discussed.

2.5.1 Semi-Permeable Membrane Devices (SPMD)

At the end of the last century, with growing environmental concern regarding the levels of POPs in water systems, a new method for sampling of the marine environment was invented to address some of the issues with traditional environmental sampling methods. Amongst the concerns at this time were sensitivity issues with regard to trace contaminant levels (< 1 ppb) found in waters and the limitations of the use of monitor organisms in environmental analysis.[94,127] Soedergren *et al.* [128] used the first type of

marine passive sampler in 1987 by incorporating the inherent benefits of a bi-phasic contaminant accumulation system *i.e*. a hydrophilic dialysis bag made of cellulose filled with hexane, which mimicked the uptake of contaminants by aquatic monitor organisms. This technique could be used to improve on sensitivity issues as well as the draw backs of using bio-monitor organisms such as lipid corrections and organism health.[94, 128]

The semipermeable membrane device (SPMD) was invented by Huckins *et al.* [94] and comprised a polyethylene tube containing carp lipid, sampled in carp from a control pond. Further modifications of the promising technique showed that the use of triolein, a synthetic lipid, improved the system.[129] Triolein is a receiving phase which exhibits a high capacity for compounds with Log K_{ow} values > 3. Since then there have been many published papers on the application of SPMDs to sample truly dissolved levels of contaminants in the marine environment.[88,130, 127, 131, 91,117,132]

2.5.1.1 Calculation of the Sampling Rate

During the integrative uptake phase the ambient chemical concentration (C_w) is determined by the following equation:

$$C_w = \frac{M_s(t)}{R_s t} \qquad \text{Eqn.2.8}$$

Where $M_s(t)$ is the mass of the contaminant accumulated by the sampler over time (t) and the dissolved water concentration (C_w) is calculated using the sampling rate (R_s).[133] For the SPMDs, some regression models have been used which can estimate a chemical's site specific R_s and its C_w based on the Log K_{ow} of the chemical, the PRC's release rate constant (k_e) and SPMD-water partition coefficient (K_{pw}). The release rate

of a PRC is determined by comparison of the amount of PRC initially added to the SPMD (N_o) and the amount remaining (N_t) as shown in *Eqn.2.9*, where the *Log* K_{pw} is determined from a regression model of the PRC's Log K_{ow} as shown using the empirically derived *Eqn.2.10* where a_0 is the intercept determined to be -2.61 for PCBs, OCs and PAHs.

$$K_e = \frac{\left[\ln\left(\frac{N_t}{N_0}\right)\right]}{t} \qquad \text{Eqn.2.9}$$

$$LogK_{pw} = a_o + 2.321\log k_{ow} - 0.1618(\log k_{ow})^2 \qquad \text{Eqn.2.10}$$

The sampling rate for PRCs can then be calculated as shown in *Eqn.2.11* where V_s is the volume of the SPMD (in L or mL).

$$R_s = V_s K_{pw} k_e \qquad \text{Eqn.2.11}$$

The extrapolation of C_w from measured values of N requires knowledge of a chemical's site-specific sampling rate (R_s) which is determined from a third-order polynomial (*Eqn.2.13*) where $\alpha_{(i/PRC)}$ is the compound-specific effect on the sampling rate and the relation between the $R_{s\text{-}PRC}$ and R_s (*Eqn.2.12*).

$$Log\,\alpha_{(i/PRC)} = 0.0130\log K_{ow}{}^3 - 0.3173\log K_{ow}{}^2 + 2.244\log K_{ow} \qquad \text{Eqn.2.12}$$

$$R_s = R_{s-PRC}\left(\frac{\alpha_i}{\alpha_{PRC}}\right) \qquad \text{Eqn.2.13}$$

2.5.1.2 Calculation of the Dissolved Water Concentration

The dissolved water concentration C_w can then be calculated using the equation below (*Eqn.2.14*):

$$C_w = \left(\frac{N}{V_s K_{pw} \left[1 - \exp\left(\frac{-R_s t}{V_s K_{pw}} \right) \right]} \right) \qquad \text{Eqn.2.14}$$

The calculations described above are used where PRCs have been spiked into the sampler and R_s and C_w concentration can be calculated accordingly, however in the cases where PRCs have not been used a laboratory derived compound specific sampling rate is needed to derive the C_w. [133]

2.5.2 PDMS Passive Samplers

Early validation of SPMD PSDs showed that virtually any material with a non-polar structure can function as a passive sampler.[89,103] PDMS was subsequently shown to be an excellent passive sampler material by the RIKZ in the Netherlands because of a high partition co-efficient and low transport resistance with only a few known disadvantages.[103] Also the single phase sampler is easy to construct, easily spiked with PRCs and offers a simplified version of the modelling of contaminant uptake over the bi-phasic SPMD.[118] Silicon rubber PS devices are fast becoming increasingly relevant with respect to monitoring of non-polar organic compounds. This is an ongoing research area and the continued development of silicon rubber samplers has increased confidence in their application.

2.5.2.1 Calculation of Sampling Rate (R_s)

The *in situ Rs* was calculated using the PRC data that was judged as acceptable for further processing using the following formula (*Eqn.2.15*):

$$\frac{N_t}{N_0} = \exp\left[-\frac{R_s t}{k_{pw} m}\right] \qquad \text{Eqn.2.15}$$

Where N_o is the concentration for the PRC found in the preparation control, N_t is the concentration found in the exposed sampler. R_s is the *in-situ* sampling rate, t is the exposure time in days, k_{pw} is the passive sampler-water partition coefficient and m is the mass of the passive sampler after extraction. As previously discussed, where PDMS passive samplers were deployed in inshore and marine locations in saltwater the salting out affect on the passive sampler – water partition coefficient (K_{pw}) was determined using the following formula:

$$LogK_{pw}^{so} = LogK_{pw}^{so} + k_s I \qquad \text{Eqn.2.16}$$

Where *Log* K_{pw} is the passive sampler-water partition coefficient, I is the molar ionic strength, *Log* K_{pw}^{0} is the partition coefficient at $I = 0$, k_s is the Setschenow[114] constant *Log* K_{pw} and *Log* K_{pw}^{so} values used in this study are shown in appendix A.1. The magnitude of the R_s has been shown to be controlled by the water boundary layer (WBL)[118] and weakly decreases with increasing molecular weight. Hence a proportionality constant (B) is used and can be calculated using the following formula (*Eqn.2.17*):

$$R_s = \frac{B}{M^{0.47}} \qquad \text{Eqn.2.17}$$

Where *B* is the proportionality constant and $M^{0.47}$ is the molar mass to the power of 0.47 as estimated using experimental values. Booij has shown that as the constant *B* is difficult to understand it made sense to calculate the sampling rate for a compound with a median molar mass (300 g mol^{-1} was chosen). [119] By combining *Eqn.2.16* and *2.17* the sampling rate can be estimated using the following (*Eqn.2.18*):

$$\frac{N_t}{N_0} = \exp\left[-\frac{B\,t}{k_{pw} M^{0.47} m}\right] \qquad \text{Eqn.2.18}$$

The constant *B* was further calculated by fitting N_t/N_0 as a function of $Log(K_{pw}\ M^{0.47})$ against the retained PRC fraction and using un-weighted non-linear least squares to calculate *B* as shown by Booij.[119] Once *B* had been calculated it was converted to the R_s using equation 2.17.

2.5.2.2 Calculation of the Dissolved Water (C_w) Concentration

For estimation of the freely dissolved water concentration found by the passive sampler sheets the full uptake is described by the following formula (*Eqn.2.19*) which is derived from the general equation shown (*Eqn 2.14*):

$$C_w = \frac{N_t}{K_{pw} m \left[1 - \exp\left[- \frac{Bt}{K_{pw} M^{0.47} m} \right] \right]} \qquad \text{Eqn.2.19}$$

Where C_w is the dissolved water concentration of contaminants (pg/L), N_t is the membrane concentration per weight of sheets found (ng per sample), K_{pw} is the passive sampler water partition coefficient, m is the mass of the membrane in kg, B is the proportionality constant and $M^{0.47}$ is the molar mass to the power of 0.47.

2.6 A Role for Passive Sampling in the WFD?

When concentrations of substances in the surface water are so low that they can no longer be detected with the classical monitoring methods, measuring concentrations in biota is used as an alternative. The WFD permits monitoring with biota in certain cases once methods and relevant standards are generated.[134]

The WFD guidance document for surface waters [11] states that passive sampling can be used alongside spot sampling to confirm or refute the results of spot sampling. Thus as the calculation of annual average concentrations is key to the WFD it is likely that as research and validation continues, the use of passive sampling for monitoring purposes, which exhibits significant promise, may become more relevant for environmental monitoring.

EQS in biota are set out for a number of compounds included in the priority substances list specifically mercury, HCB and HBCD, and are proposed for a number of substances on the current list (PBDEs and PAH) as well as a number of new substances proposed for inclusion in the WFD. Article 3 in the EQS Directive (2008/105/EC) [11] states that

long-term trend analysis of concentrations of those priority substances (listed in Part A of Annex I) that tend to accumulate in sediment and/or biota must be completed. Current research suggests that measuring contaminants in biota offers an alternative approach to water sampling.

Strong correlations between mussels and silicon rubber passive samplers for organic compounds, both in terms of concentrations measured and effects have been reported [135] thus supporting the potential for application of PDMS in support of monitoring objectives. Other PS studies have reported pollutant concentrations lower than those usually expected for most compounds in the water phase.[136] Passive sampling of sediment is promising for trend monitoring purposes as fewer problems with differences in sediment characteristics are encountered. The extent to which particulate bound contaminants are readily bioavailable to resident organisms is currently difficult to quantify.

One of the primary concerns in relation to the application of passive sampling to WFD (MSFD) monitoring is that EQSs are based on whole water concentrations while passive sampling measures freely dissolved concentrations as the samplers exclude dissolved organic matter (DOM) and suspended particulate matter (SPM).

Monitoring of chlorinated hydrocarbons (and trace metals, including mercury), in shellfish and fish has been conducted in Ireland for a number of years, in accordance with EU directives and via OSPAR and CEMP. Little is known about the concentrations of compounds with newly proposed biota EQS, which include hexachlorobenzene and PFOS among others and a gap in the knowledge currently exists. Species selection and protocols should take into account as well as WFD guidelines for monitoring in

sediment and biota and OSPAR JAMP monitoring guidelines/ICES advice for marine waters (JAMP 2003).

Smedes *et al.* [135] reports that freely dissolved concentrations determined using passive sampling with silicon rubber and concentrations in mussels correlate closely. The uptake process in partition passive sampling is largely the same as that in lower organisms such as mussels where a difference in chemical activity between the water and the mussel, or between the water and the passive sampler, results in the uptake of a substance. In both cases, equilibrium with the water phase may be achieved over time. In addition to uptake through direct contact with water as determined by partition, organisms can also accumulate substances through food. Substances in food from the same water in which the organism itself is located will have the same chemical activity as in the water. This indicates that the food will contribute to the faster uptake of the substances by the organism than by the passive sampler which does not ingest the food. This means only that the mussel will be in equilibrium with the substances in the water phase faster, not that the chemical activity will be higher. The matching chemical activity in the food means that the growth of an organism does not result in 'dilution' and a lower concentration. Smedes *et al.* [135] report contents in mussels, that grow by up to a factor of two during exposure, and in mussels that did not grow or even reduced in size had the same ratio to the freely dissolved concentration based on passive sampling.[89]

Smedes *et al.* [89] further conclude that the bioaccumulation factor (BAF), expressed as a ratio between lipid normalised contents in mussels and freely dissolved concentrations in water, can (with some exceptions *e.g.* natural variation) be used to predict contents in mussels using passive sampling data. Lipid-water BAFs are closely linked to the K_{ow}

for lower organisms that primarily accumulate substances from the water phase than for organisms on a higher trophic level contaminants can accumulate via biomagnification. This process being a complicated combination of factors (including amongst others, chemical properties, lipid content in the animal (and in the prey). organism response and metabolic/release of compounds). A recent study comparing passive sampling with biomonitoring data for zebra mussels, eels and the common roach in various Dutch waters found bioaccumulation factors (BAFs) that deviated only slightly from the K_{ow}.[137] Good BAF values (best for PCBs) were not found for all compounds but a number of other temporal and analytical issues as well as metabolism in the animals sampled may account for some of the differences.

While correlations have been established, given the associated complications, this area of research is still in development. Smedes *et al.* [135] conclude that passive sampling will never be able to generate a precise prediction of contents in an organism. Living organisms are dynamic and they respond to all sorts of factors that do not affect passive samplers. Ultimately the authors report a number of benefits of passive sampling as compared to bio-monitoring including:

- Passive samplers remain in fixed positions and do not move into other areas;
- Passive samplers do not metabolise pollutants and so a measurement of the actual exposure is obtained;
- The same passive samplers can be used in fresh, marine, cold and warm water; with bio-monitoring, the selection of the organism depends on the matrix (fresh or marine) and the environmental conditions;
- Passive samplers also work in anoxic or even toxic water in which organisms cannot survive;

- Passive sampling results are comparable on the global scale, on condition that they are conducted in comparable ways;
- By contrast with organisms deployed as bio-monitors, passive samplers do not have initial concentrations;
- No organisms need to be sacrificed when passive sampling is used;
- No separate standards need to be set for passive sampling.

2.6.1 Overall Conclusions and Recommendations Regarding Passive Sampling.

It can be concluded from the preceding sections that passive sampling is not specifically mentioned as a monitoring method in the Water Framework Directive and/or in relation to Irish implementation of the WFD. [4]

The fact that the guidance document on surface water chemical monitoring [11] does refer to passive sampling (in the case of this work PDMS) as a complementary method that can be used for both monitoring network design and surveillance monitoring is key to ongoing efforts to continue research to further fully validate (*e.g.* to EN ISO/IEC-17025 or other equivalent standards) the various techniques employed.

A possible way of circumventing this difficulty is the fact that, when no analysis methods are available that fulfill the minimum 'performance criteria', the best available techniques not entailing excessive costs must be used. Passive sampling may be the best available technique for very low concentrations that are not detectable in water samples obtained in the traditional way.

In addition, passive sampling can also be used in parallel with spot sampling in order to confirm or refute the results for water samples taken in the traditional way, particularly in situations in which contaminant concentrations fluctuate considerably over time. Passive sampling can also play this role in investigative monitoring. An ongoing issue is that the compliance checking of water quality under the WFD with respect to organic compounds is based on total water concentrations and that passive sampling measures the freely dissolved (bio-available) concentration. However, total concentrations in water can be calculated using averaged measured DOC concentrations, suspended matter and total organic matter with equilibrium partitioning on the basis of the freely dissolved concentration determined with passive sampling. The main advantage of passive sampling is that it measures exactly what is needed for risk assessments, which is the freely dissolved water concentration. Another major advantage of the freely dissolved concentrations in the water phase is that, by contrast with concentrations in total water, they no longer need to be corrected for local conditions such as concentrations of suspended matter and DOC. Passive sampling with silicon rubber has been found to perform excellently for a wide range of compounds in the marine environment thus the time would therefore seem to be ripe to use silicon rubber more in WFD monitoring.

Chapter 3: Experimental Method Development and Validation for all Analysed Matrices

3.1 Introduction

Chapter 3 documents all elements of method development and validation incorporating instrumental choice and performance, in addition to the extraction and analysis of all the matrices employed in this project. Each matrix including PSDs (PDMS), biota (eel and trout) and sediment had method development tailored for a range of POPs as part of this study with details of the type of extraction and instrumental analysis shown in *Table 3.1*.

Method development and validation followed a sequential process from the initial detailing of instrumental performance parameters through to full sample extraction cleanup and analysis ultimately leading to development of method quality assurance procedures to ensure that individual methods were fit for purpose. It should be noted that where subcontract laboratories (Eurofins Gmbh, IVM) were employed these were selected on the basis of long-term experience (peer reviewed publications) in the relevant field, and their performance in international proficiency studies where relevant. Overall optimisation and validation for all POP methods followed the same general pathway with a number of common steps incorporating;

1) Selection of relevant instrumentation.
2) Assessing instrumental performance;
    a) Summary of instrumentation employed (GC-ECD and GC-MS);
    b) Relevant validation parameters (repeatability, accuracy, precision, linearity and limit of detection/quantification (LOD/LOQ);
    c) Identification of analytes involved using individual standards;
    d) Identification of all analytes in solution;

e) Preparation and testing of calibration standards;

f) Validation of instrumental parameters.

3) Full method development/validation for biota and sediment and PSD;

a) Identification of appropriate extraction method;

b) Initial testing using materials with known analyte concentrations;

c) Submission of results to QUASIMEME testing scheme.

Overall final method performance for biota and sediment was validated by successful participation in the quality assurance of information for the marine environment (QUAISMEME) proficiency testing scheme. This scheme involves the transporting of testing materials (marine biota and sediment) to participant laboratories. The laboratory in question then extracts and analyses the samples using their own in house techniques and returns data to QUASIMEME where they are assessed and a score is assigned depending on the closeness of agreement between the final result reported by the participant laboratory and the result calculated by QUASIMEME.

In the case of passive sampling overall quality assurance of the data generated consisted of comparisons to concentrations reported in biota from the same area, comparison of samplers deployed in unison at a particular site and finally by participation in the network of monitoring and related organisations and bio-monitoring of emerging environmental (NORMAN) pollutants inter-calibration exercise. Critical assessment of all passive sampler results also contributed to overall quality assurance and this included comparison to field and laboratory controls calculated concentrations and limit of detection calculations.

Table 3.1 List of methods and instrumentation employed in the extraction and analysis of all matrices analysed in this study

Parameter	Passive samplers	Biota	Sediment
PAH	Soxhlet Extraction/MS analysis (Section 3.5.1.)	Smedes extraction - MS Detection (section 3.4.2)	Soxhlet extraction - MS Detection (section 3.4.1)
PCB	Soxhlet Extraction/ECD analysis for chapters 4, 5 and 1st deployment chatper 6 (Section 3.5.1.)	Smedes extraction - MS Detection (section 3.4.2)	Soxhlet extraction - MS Detection (section 3.4.1)
OC	Soxhlet Extraction/ECD analysis for chapters 4, 5 and 1st deployment chatper 6 (Section 3.5.1.)	Smedes extraction - MS Detection (section 3.4.2)	Soxhlet extraction - MS Detection (section 3.4.1)
PBDE	Soxhlet Extraction/MS analysis (Section 3.5.1.)	Smedes extraction - MS Detection (section 3.4.2)	Soxhlet extraction - MS Detection (section 3.4.1)
PCA/PCP	N/A	IVM analysis	IVM analysis
PCDD/F	Eurofins analysis	Eurofins analysis	Eurofins analysis

3.1.1 Measurement of POPs in Marine Matrices

While a number of different analytical techniques are now readily available to the analytical chemist, the analysis of hydrophobic POPs in marine matrices is generally carried out using gas chromatography coupled to a variety of detection methodologies or in the case of PAHs by HPLC based separation techniques coupled with detection techniques including either fluorescence or mass spectrometry.[138,139,140]

Gas Chromatography in conjunction with electron capture detection (ECD) and/or mass spectrometric detection (MS) is now an established technique for the analysis of PCBs, OCs, PBDEs and PAHs in marine matrices primarily because of its high sensitivity (*e.g.* ECD especially for halogenated compounds) and high selectivity in the case of MS based methods.[141,26]

As levels of POPs in the Irish marine environment are generally low the analysis of sediment, biota and PSDs all require levels of analytical specificity and sensitivity that can be offered by both of these techniques. It is not the purpose of this study to exhaustively review the current state of knowledge in respect of the analysis of POPs in marine matrices, thus summary details of GC-ECD/MS instrumental parameters employed during this study are reported below with further GC-MS details shown in appendix A.3.

A gas chromatograph consisting of an oven, gas supply and flow controllers, injector and chromatographic column is common to both MS and ECD detection techniques with the sample being volatilised by injection into the liner of the inlet via the injector

port, which is heated, where it mixes with a relevant carrier gas (*e.g.* helium/hydrogen) which carries the volatilised compounds on to the analytical column. Resolution of compounds is then brought about primarily based upon their chemical properties, their interaction with the selected stationary phase and as a function of the temperature of the column oven which all facilitate separation and elution from the column at different time intervals.

In the case of the MS, the GC is connected to the MS section through the transfer line which was heated to 300 ^{o}C (*Fig 3.1)*. The volatilised compounds are transferred through this line into the ionisation source (typically a tungsten filament) where they are ionised and fragmented before being focused using lenses. The ions are then accelerated into the mass analyser region where they are separated by their mass to charge (*m/z*) ratio using electromagnetic fields generated by the quadrupole before being detected based on their *m/z* ratio.

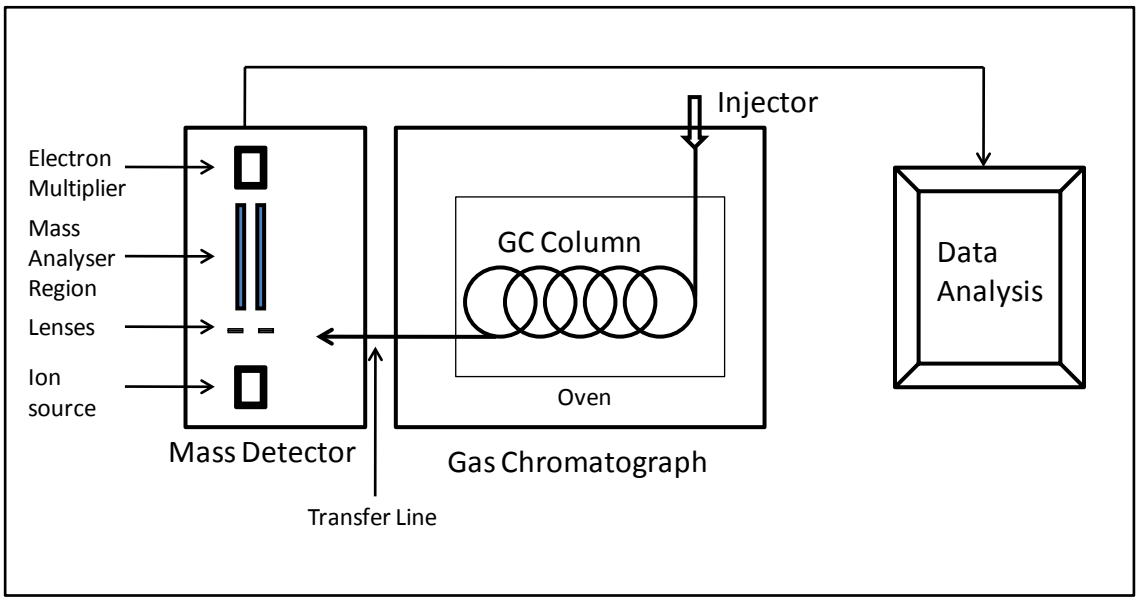


Figure 3.1 A block diagram of a typical gas chromatograph/mass spectrometer detector. [142]

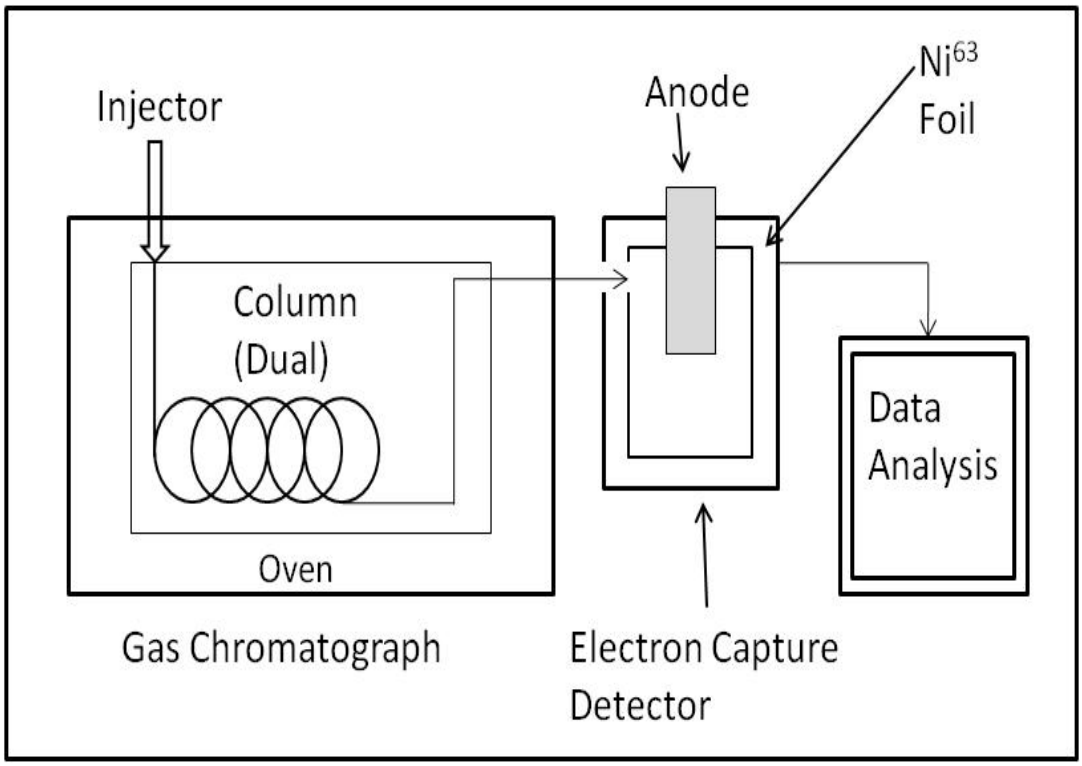


Figure 3.2 A block Diagram of a typical gas chromatograph with electron capture detector. [142]

In the case of the ECD (*Fig 3.2*) eluting compounds enter the electron capture detector where they are bombarded by electrons from the radioactive source (Ni^{63}).[142] A potential difference is applied to the ECD cell which allows the capture of negatively charged electrons and by ionisation of a moderating gas (nitrogen) creates a base line signal. When a molecule, with the ability to capture an electron enters the cell it changes the current in the cell. The degree of current change becomes the detector signal which is processed by the recorder and becomes a peak on the corresponding chromatogram. [142]

3.1.2 Relevant Validation Parameters

Method validation can be defined as "the confirmation, by experimentation and the provision of objective evidence, that the requirements for a specified use are fulfilled" [143] hence the validation process was based on the repeated determination of a range of

performance characteristics including instrument specificity, linearity, limit of detection (LOD), limit of quantification (LOQ), accuracy, precision and Uncertainty of Measurment (UCM). Also included are the use of QUASIMEME samples for the analysis of sediments and biota which, while not certified, do provide materials of a suitable composition and analyte concentration to provide a measure of quality assurance and quality control of the instrumentation, and the extractive/preparative steps involved in instrumental analysis. The following sections provide brief information on the various performance characteristics while appendix A.4 illustrates the data generated for selected POPs (PCB and PAH).

3.1.2.1 Specificity

Specificity can be defined as the ability to measure accurately and specifically the analyte of interest in the presence of other components which may be present in the sample matrix or the ability to assess unequivocally the analyte in the presence of components which may be expected to be present.[143] The GC-MS when used in SIM mode provides a high degree of selectivity as the specific ions used in the SIM method are used to 'scan' the sample meaning only those compounds of interest are detected. For the GC-ECD run in dual column mode a high degree of selectivity is also conferred. While not as specific as the GC-MS the use of retention time variation and relative retention time are used to satisfy specificity for the GC-ECD (appendix A.4 *Table 1*).

3.1.2.2 Accuracy

The accuracy of an analytical process can be defined as a measure of the closeness of agreement between the value which has been accepted as a true value or accepted value and a value calculated from the analysis.[143] In this case instrumental accuracy is

satisfied by analysing standards of known concentration while overall accuracy can be satisfied using QUASIMEME reference materials. Results for sediment and biota QUASIMEMEs are shown in section 3.4.1 and 3.4.2 along with instrumental quality control in appendix A.4 *Table 1*.

3.1.2.3 Precision

Precision can be defined as the closeness of agreement (degree of scatter) between a series of measurements obtained from multiple analysis of the same homogeneous sample under the conditions of the method.[144] Precision can be a function of, or independent of, analyte concentration or value and is also matrix dependent. Precision can be calculated as a percentage relative standard deviation from the results of replicate analysis, for a given set of conditions. In this case instrumental precision was calculated by repeated injection of standards with results shown in appendix A.4 *Table 1* while overall precision was satisfied using QUASIMEME results shown in section 3.4.1 and 3.4.2.

3.1.2.4 Linearity

Linearity can be defined as the ability of a method to show results that are directly proportional to the analyte concentration range.[143] In this case the linear range can be adjudged as the range of standard analyte concentration over which the method gives test results which are proportional to the concentration of the analyte. Linearity across the range of standards can be deemed as satisfied if the r^2 value calculated for a set of calibration standards analysed using the instrument is >0.995. Results are shown in appendix A.4 *Table 1*.

3.1.2.5 Limit Of Detection /Limit Of Quantification

The instrumental LOD for any analytical procedure can be defined as the point where it is difficult to be certain that any signal being received by the instrument for an analyte arises from the analyte and not the background.[143] In this study the LOD was calculated by using the instrument average response for repeated analysis of the sample blank. The calculated response +3SD was deemed acceptable as the LOD in this case. The instrumental LOQ can be defined as the lowest concentration that can be determined with an expectable level of precision and accuracy under stated laboratory conditions. In this study the LOQ was calculated by taking the average instrument response of individual analytes for a series of sample blanks +7SD.[143] Results are shown in appendix A.4 *Table 2*.

3.1.2.6 Robustness

Robustness, sometimes referred to as ruggedness is often described as a set of experiments which can allow an analyst to identify the experimental parameters which can have an effect on the method. Robustness for this study can be considered satisfied in that for biota and sediment analysis, repeated extraction and analysis of materials by a number of analysts for a number of years using the same methods as described (section 3.4.1 and 3.4.2) results in little deviation which indicates that the method is sufficiently robust. For passive sampling the extraction and analysis of materials took place in accordance with methods set out by Smedes *et al.* [115] and have been used for more than a decade by a variety of analysts to extract and analyse passive samplers.

3.1.2.7 Uncertainty of Measurement

Uncertainty of measurement (UCM) relates to the doubt that exists about the result of any measurement.[143] For this thesis UCM calculations were completed based on the Nordtest method using replicates of biota (QUASIMEME) proficiency testing materials.[145] The Nordtest method incorporates within laboratory reproducibility and bias to estimate a combined uncertainty value (%). An example of UCM estimated for this thesis (with coverage factor of 2 – 95 % confidence interval) for biota (QOR099BT n = 17) is at an upper level of 20.6 % for PCBs and is shown in appendix A.4 *Table 3*. UCM details for other analytes analysed as part of this study are shown in appendix A.4 *Table 1*. In the absence of a reference material for PDMS these estimates can give upper guidance on the level of UCM. These figures provide an estimate (as above) on analytical measurement however one of the major UCM issues for passive sampling lies in the generation of the sampling rate and in the *Log* K_{pw} value used. Smedes *et al.* [146] suggest that *Log* K_{pw} values used in different studies can vary up to 0.55 log units which can have an effect on subsequent R_s and final C_w calculations. This project did not further evaluate this component in relation to passive samplers however the uncertainty inherent in passive sampler estimations is further covered in the literature by Lohmann *et al.* [147]

3.2 Instrument Method Optimisation/Validation

Method development and validation required for analysis of various matrices (sediment, passive samplers and Biota) proceeded in a stepwise manner. In the case of biota and sediment the ultimate aim of assessing “fitness for purpose” was via successful participation using the methods developed in a recognised international proficiency testing scheme (QUASIMEME). PSDs used in this study currently do not have a

proficiency study associated with them however utilisation of PDMS materials from an inter-calibration exercise (NORMAN) was used to support PSD measurements.

Quantification of PAH, PCB/OCs/PDBEs in all matrices (sediment, biota and PDMS) was either performed using the Agilent GC-MS and/or Varian 1200 GC-ECD.

3.2.1 GC-MS Method Development/Validation

Method development of the GC-MS parameters proceeded as outlined in section 3.1 where individual POP standards were injected first for identification purposes before a mixture containing all compounds was used to optimise the GC-MS parameters to ensure good chromatographic separation and subsequently ease of identification. Individual standards were analysed using the GC-MS run in scan mode where the instrument 'scanned' for any peak with a *m/z* ratio between 50 and 500 AMU (higher for BFRs). The data recorded from this analysis were primarily and most importantly, the identification ions generated for each compound of interest, but also the approximate retention time and the order of elution. Once all the compounds had been analysed and identified it was then possible to run a standard solution containing all the compounds of interest and establish their final elution order in relation to each other.

3.2.1.1 Optimisation of GC-MS Parameters

Once all compounds had been identified it was then possible to optimise all of the GC-MS instrumental parameters to ensure that good chromatographic separation was achieved. This involved changing various parameters such as the column oven temperature programme and carrier gas flow parameters. Method optimisation was

completed for POPs using an Agilent 6890 gas chromatogram coupled to a 5973N mass spectrometer.

The MS operating parameters for PAHs as an example are shown below (*Table 3.2*) with operating methods for all compounds (PBDE, PCB and OC) shown in appendix A.3 *Table 1* and *2*. Once this was complete it was then possible to set up a single ion monitoring (SIM) programme to improve the resolution and remove potential noise in the subsequently analysed samples.

Table 3.2 GC-MS optimised method parameters for the analysis of PAHs in all matrices.

Instrument	Parameter
GC Model	Agilent 6890 GC coupled to 5973 MSD
Carrier Gas	Helium
Flow rate	1.0 ml/min
Column	Agilent DB-5, 60 m, 0.250 mm x 0.25 µm
Detector	Mass spectrum detector
Injection parameters	
Injection method	Splitless
Temperature	250 ^{o}C
Syringe	Agilent 10 µl Gold Standard
Injection volume	5 µl
Liner	Agilent Liner part No: 5062-3587
Detector parameters	
Method	Electron ionisation
Ion source Temperature	230 ^{o}C
Auxilary Line 2 Temperature	300 ^{o}C
MS Quad Temperature	150 ^{o}C

3.2.1.2 GC-MS Single Ion Monitoring (SIM) Method.

All POPs of interest to this study were first identified using the retention times and identifying ions of individual standards which were analysed using the GC-MS in scan mode (50-550 *m/z*). The data generated from the GC-MS ion scan was then used to generate a SIM programme which allows the GC-MS look for individual ions during the analysis programme at the retention time that they are expected to elute. Using SIM techniques improves the selectivity, accuracy and sensitivity of the instrument while reducing background noise and interfering co-eluting peaks. Standards containing mixtures of contaminants of interest to this study (PCBs, OCs, PAHs and PBDEs) were analysed by the GC-MS again using the parameters outlined in appendix A.3 *Table 1* and *2* with those used to analyse PAHs shown below (*Table 3.3*) as an example. The injection of the PAH standard 1 (1000 ng/g) with added internal standard (PAH mix 24D 10 ng/µl) resulted in the chromatogram shown below (*Fig. 3.3.*)

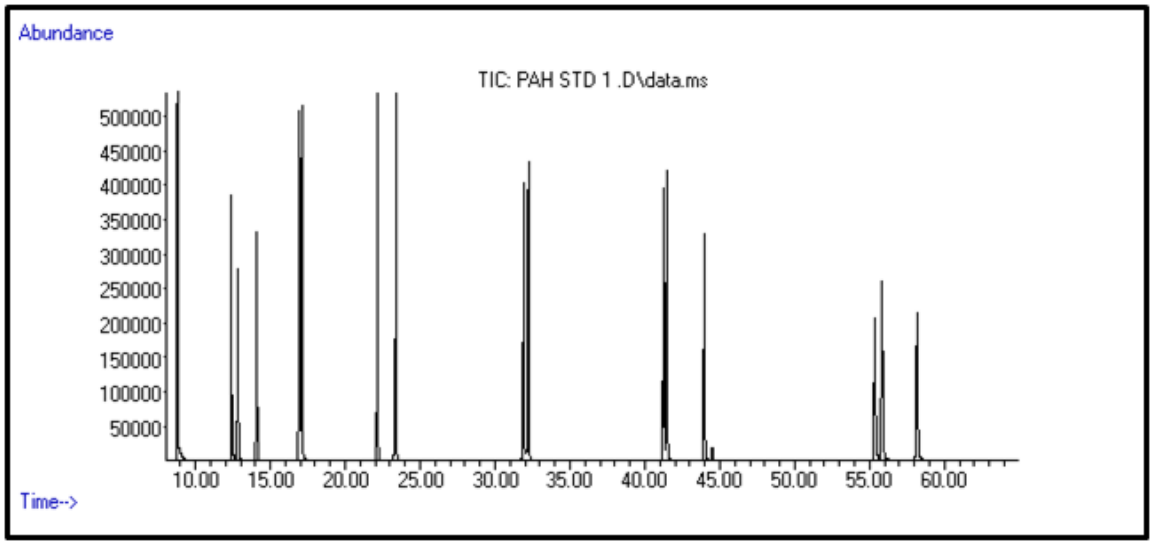


Figure 3.3 SIM Chromatogram of PAH Standard (STD 1 - 1000 ng/g) analysed on the GC-MS with conditions as detailed in Tables 3.2 and 3.3 with all 16 US EPA listed priority pollutants present.

Table 3.3 The finalised SIM method sequence showing the segment (Seg) number containing the retention time (R_t) and the identifying ions used to isolate each PAH along with the associated internal standard using the GC-MS.

Compound	Ion	Retention time (mins)	Internal standard	Segment	
				Seg	Start time (mins)
Naphthalene	128	8.81	naphthalene d_8	1	8.00
Acenaphthylene	152	12.38	acenaphthene d_{10}	2	11.00
Acenaphthene	153	12.82	acenaphthene d_{10}	3	12.60
Fluorene	166	14.09	acenaphthene d_{10}	4	13.50
Phenanthrene	178	16.96	phenenthrene d_{10}	5	15.00
Anthracene	178	17.22	phenenthrene d_{10}		
Fluoranthene	202	22.14	phenenthrene d_{10}	6	22.00
Pyrene	202	23.36	phenenthrene d_{10}		
Chrysene	228	31.87	chrysene d_{12}	7	28.00
Benzo(a)anthracene	228	32.20	chrysene d_{12}		
Benzo(b)fluoranthene	252	41.18	chrysene d_{12}	8	37.00
Benzo(k)fluoranthene	252	41.42	chrysene d_{12}		
Benzo(a)pyrene	252	43.90	chrysene d_{12}		
Indeno(1,2,3-c,d)pyrene	276	55.29	perylene d_{12}	9	47.00
Benzo(g,h,i)perylene	278	55.75	perylene d_{12}		
Dibenzo(a,h)anthracene	276	58.09	perylene d_{12}		

3.2.2 GC-ECD Method Development/Validation

The GC-ECD method optimisation was completed on a Varian 3800 gas chromatograph using a dual column system and a Ni^{63} source electron capture detector. A dual column system was employed in this case to prevent co-elution of peaks as a large number of contaminants were analysed. Both CP-SIL 19 and HT8 columns (details in *Table 3.4*) contained different stationary phases which interacted with the compounds of interest in a differential manner with the intention of providing an alternative analytical value when co-elution was an issue. Where this did occur on one column, quantification could be completed using the other column. Optimisation proceeded in line with the procedure outlined in section 3.1. A standard containing all PCBs and a separate standard containing OCs as well as individual reference standards for both types of compound were purchased from CPI International. Individual standards of PCB and OC

compounds were first run on the GC-ECD to check their retention time. Once the individual standards had been analysed a mixture of all PCBs and a mixture of all OCs was then analysed in a similar manner. Problems with co-eluting compounds were noted before GC-ECD parameters were optimised to ensure good chromatographic separation of all compounds on both columns. The final GC-ECD instrumentation set up for PCBs and OCs is shown below (*Table 3.4*).

Table 3.4 GC-ECD optimised method parameters for the analysis of PCBs/OCPs in all matrices

Instrument	Parameter
GC Model	Varian 3800 GC with ECD detector
Carrier Gas	Hydrogen (generator)
Flow rate	1.4 ml/min
Columns	SGE-HT8 50 m x 0.22mm x 0.25 µm
	Varian CP SIL 19 60 m x 0.25 mm x 0.25 µm
Detector	Ni^{63} source electron capture detector
Injection	
Injection method	Splitless
Temperature	240 ^{o}C
Syringe	Hamilton 701 NPT 5 10 µl
Injection volume	2 µl
Liner	SGE 3.4 mm single taper
Detector	
Method	Electron capture detection
Temperature	280 ^{o}C
Gas	Nitrogen

Once this was completed the retention times for both columns were noted and as can be seen in below (*Table 3.5*) are adequately different to allow co-elution issues be resolved. The GC-ECD dual column set up is complex in that the sample is injected into one injection port where both columns are placed. The volatile compounds are heated

up and forced on to both columns simultaneously under the influence of the mobile phase (hydrogen). The columns are attached to separate detectors allowing simultaneous sample analysis. However this set up doubles the integration and quantification work involved in analysis of the samples. Retention times of PCBs as an example on both ECD channels (front and middle) are shown below (*Table 3.5*) with a chromatogram (*Fig 3.4*) showing the elution of PCBs in standard 1 (40 ng/g^{-1}) on the front channel.

Table 3.5 Retention time for each PCB and two OCs (pp-DDE and HCB) measured using the GC-ECD analysed under optimised conditions for the Front (CP-SIL 19) and Middle (HT8) columns.

	Front Column		Middle column
Compound	**Time (mins)**	**Compound**	**Time (mins)**
HCB	10.6	HCB	13.0
PCB 18	12.7	PCB 18	10.1
PCB 31	14.8	PCB 31	17.0
PCB 28	14.8	PCB 28	17.3
PCB 52	16.8	PCB 52	19.1
PCB 44	18.4	PCB 44	20.8
PCB 101	22.2	PCB 101	25.9
PPDDE	24.7	PPDDE	28.0
PCB 149	26.6	PCB 149	30.4
PCB 118	27.1	PCB 118	31.5
PCB 153	28.3	PCB 153	33.0
PCB 105	29.7	PCB 105	33.9
PCB 138	30.9	PCB 138	34.9
PCB 156	34.6	PCB 156	38.4
PCB 180	35.1	PCB 180	38.8
PCB 170	37.0	PCB 170	40.4
PCB 194	40.0	PCB 194	44.8
PCB 209	42.5	PCB 209	47.9

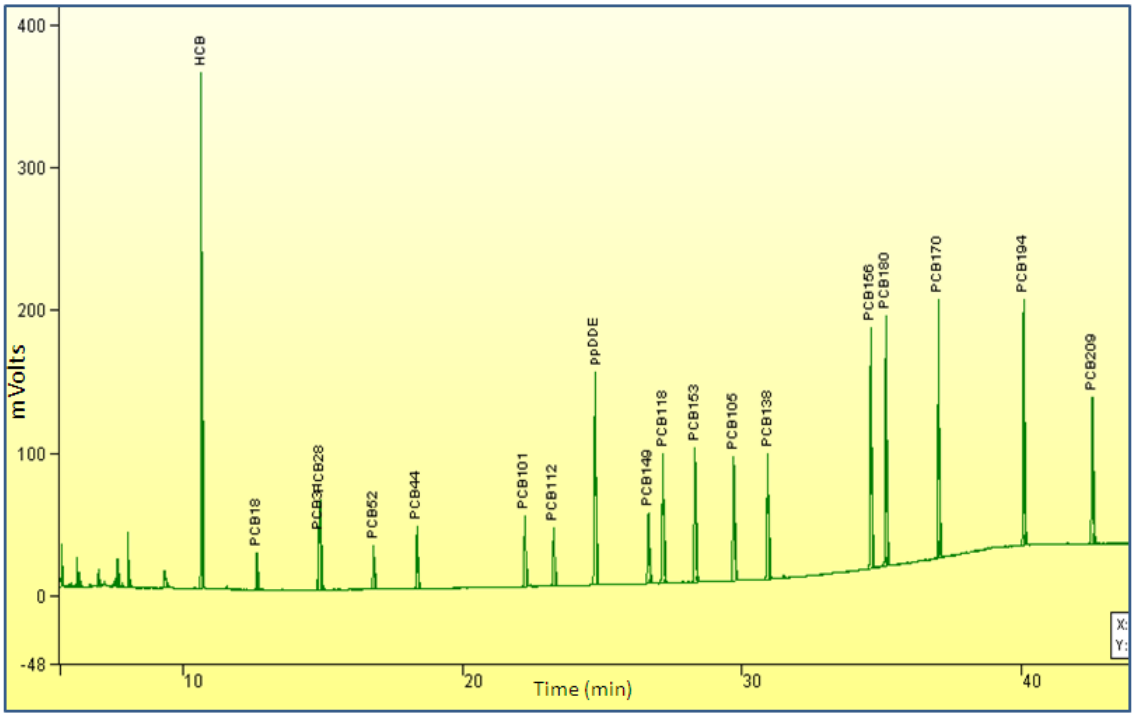


Figure 3.4 Chromatogram showing all PCBs analysed on the GC-ECD using an analytical standard (STD 1 - 40 ng/g) and the CIP SIL 19 column under conditions as set out in *Table 3.4*

3.3 Preparation of Calibration Standards

During the course of this study there were a number of sets of calibration standards created. The preparation of PAH standards are included as an example of the procedure involved in this preparation. Using the purchased PAH mix 9 (10 ng/µl) (Ehrenstorfer, US) a series of calibration standards was created using serial dilution with an internal standard. Using PAH mix 9, working stock 1 was produced by weighing out 610 mg of the PAH mix 9 mix and adding to 3000 mg of 2,2,4-trimethylpentane (isooctane). Hence working stock 1 had a concentration of 2167 ng/g. Standard 1 is created by taking 1500 mg of working stock 1 by weight and adding to 1500 mg of 2,2,4-trimethylpentane which gives standard 1 an effective concentration of 1084 ng/g. Standard 2 is created by taking 1500 mg of standard 1 and again diluting with 1500 mg of 2,2,4-trimethylpentane giving standard 2 a concentration of 541 ng/g. Standard 3 –

10 are created in a similar manner as outlined in *Table 3.8*. The following table (*Table 3.6*) shows the calculations used in the determination of the concentration of standard 1.

Table 3.6 Calculations used in the preparation of working stock 1 and subsequent standards.

Parameter	Data
PAH mix 9	
Concentration of PAH mix 9	10 ng/µl
Density of solvent (cyclohexane)	0.779 g/cm^3
Concentration in ng/g	12836.9 ng/g
Preparation of stock 1	
Weight of PAH mix 9 added	610.02 mgs
Amount of analyte present in ng	7830.8 ng
Weight of isooctane added	3002.64 mgs
Actual concentration of stock 1	2167.60 ng/g
Preparation of standard 1	
Weight of stock 1 added	1499.84 mgs
Amount of analyte present in ng	3251.06 ng
Weight of isooctane added	1502.21 mgs
Actual concentration of Standard 1	1083.71 ng/g

3.3.1 Preparation of Internal Standard

A deuterated standard PAH mix 24D (10 ng/µl) was purchased (Ehrenstorfer, US) containing naphthalene-$_{d8}$, acenaphthalene-$_{d10}$, phenanthrene-$_{d10}$, chrysene-$_{d12}$ and perylene-$_{d12}$ which was used as an internal standard. From the stock (PAH mix 24D) 300 mg was taken and added to 3000 mg of isooctane. This gives the internal standard stock a concentration of 1166 ng/g. The calculations used are shown below (*Table 3.7*).

Table 3.7 Calculations used in the preparation of internal standard Stock.

Paramater	Data
PAH mix 24D	
Concentration of PAH mix 24D	10 ng/µl
Density of solvent (cyclohexane)	0.779 g/cm^3
Concentration in ng/g	12836.9 ng/g
Preparation of Internal Standard stock	
Weight of PAH mix 24D added	299.89 mgs
Amount of analyte present in ng	3849 ng
Weight of isooctane added	3001.10 mgs
Actual concentration of stock 1	1166 ng/g

Once this internal standard was created it was added to standards 1 - 10 that were already prepared using PAH mix 9 to create standards 1IS – 10IS. Details of this dilution scheme are shown in section 3.3.2 below and *Table 3.8*.

3.3.2 Final Standard Concentrations

Standard 1 had a concentration of 1083.71 ng/g (*Table 3.6*) and had 1200 mg taken, by weight and added to a GC vial along with 100 mg of the internal standard (1166 ng/g) working stock. The 1200 mg of standard 1 had 1083.71 ng/g present which equates to 1300 mg of solvent total present and this was diluted with 100 mgs of internal standard giving the final standard 1IS a concentration of 1000 ng/g. All subsequent standards were treated in the same manner as outlined in *Table 3.8.*

Table 3.8 Preparation of the final standards (1IS – 10IS) including internal standard used to analyse PAHs in all matrices in this study.

Standard		weight (g)	Conc of STD used ng/g	STD Final Conc ng/g
	STD 1	1.20005	1083.71	1000.00
1IS	Internal standard	0.10045		
	total	1.3005		
	STD 2	1.20065	541.81	500.01
2IS	Internal standard	0.10036		
	total	1.30101		
	STD 3	1.19974	270.71	249.49
3IS	Internal standard	0.10202		
	total	1.30176		
	STD 4	1.20006	135.33	124.81
4IS	Internal standard	0.10117		
	total	1.30123		
	STD 5	1.19989	67.64	62.36
5IS	Internal standard	0.10168		
	total	1.30157		
	STD 6	1.19989	33.81	31.20
6IS	Internal standard	0.10048		
	total	1.30037		
	STD 7	1.20032	16.9	15.59
7IS	Internal standard	0.10070		
	total	1.30102		
	STD 8	1.20014	8.45	7.79
8IS	Internal standard	0.10113		
	total	1.30127		
	STD 9	1.20010	4.22	3.90
9IS	Internal standard	0.09987		
	total	1.29997		
	STD 10	1.20003	2.11	1.95
10IS	Internal standard	0.10066		
	total	1.30069		

Standards prepared in this manner were used to analyse all matrices for the compounds required on both GC-ECD and GC-MS.

3.4 Method Development for Extraction and Analysis of all Matrices

This section deals with method development for the extraction and analysis of all matrices sampled in this project which includes sediment, biota and passive sampling devices from the different sampled areas.

3.4.1 Method Development for Sediment

The method development described here is based on the US EPA method 3540C [148] which is used for extracting non-volatile and semi-volatile organic compounds in soils, sediments and sludge. In this case the method will be used to extract and analyse PAHs and PCB/OCs from sediments. The following flow (*Fig 3.5*) chart shows how the final method was applied.

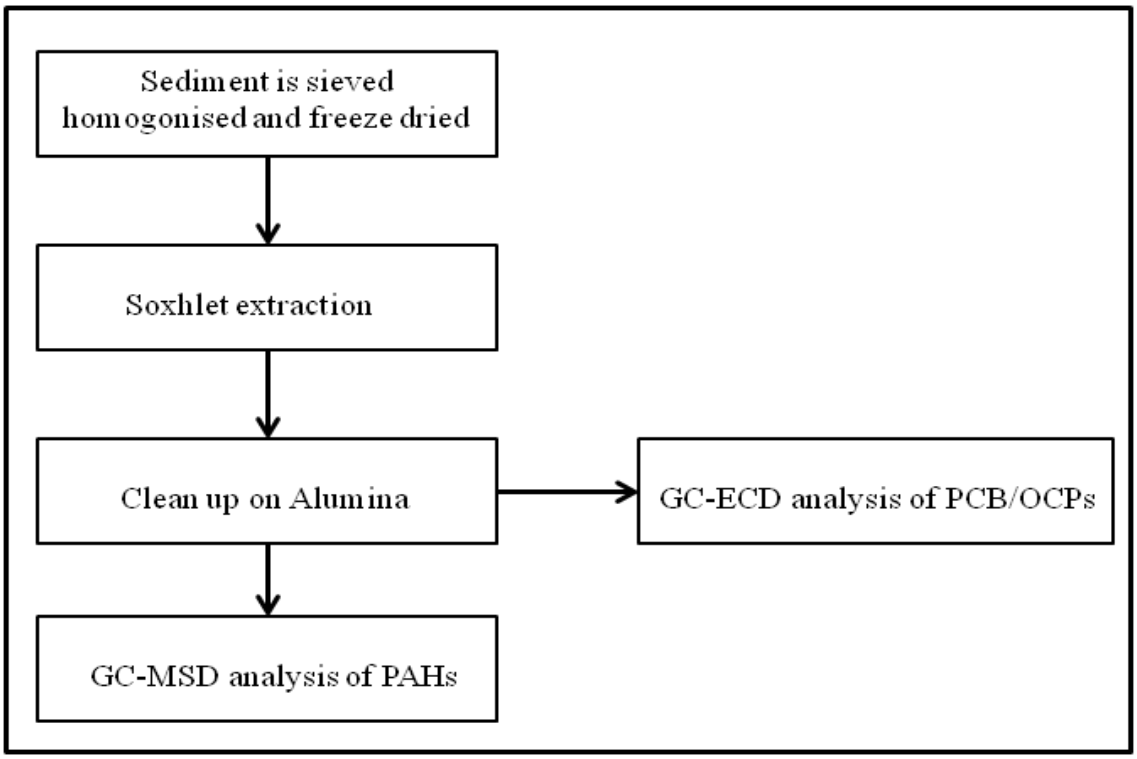


Figure 3.5 Flow chart illustrating how the extraction sequence and analysis of sediment was completed.

Sediment was collected in the field using a Van Veen sediment grab, placed in solvent washed glass jars and returned to the laboratory. The sediment was stored at -4^{o}C in a freezer before being allowed to thaw and then sieved with the 63 µm fraction retained and placed in a solvent washed sample jar. Sediment was subsequently freeze dried using a Labconco freeze drier and stored in a freezer at -28^{o}C. Before analysis could begin the samples were allowed to thaw over night. Soxhlet extraction with n-hexane/acetone was chosen as an extraction method in accordance with US EPA method 3540C.[148]

3.4.1.1 Extraction of sediment

All glassware was first cleaned in a washing machine and placed in a drying oven for 24 hours before being solvent washed a minimum of 3 times with n-hexane:acetone (1:1) before being used in the extraction procedure. Suitable CRMs and a blank were added to the sample list for extraction to ensure quality control aspects were satisfied. Sediment was weighed out (5 g approximately) and added to a glass microfiber Soxhlet bomb. The correct amount of internal standard by weight (~ 100 mg) was then added. Copper turnings were treated with concentrated HCl to remove elemental Sulphur. The turnings were cleaned 3 times using methanol, isooctane, hexane, acetone and finally hexane:acetone (1:1). Cleaned turnings were stored under hexane:acetone (1:1) before addition to the Soxhlet bomb. A clean spatula tip full of copper turnings was added into each Soxhlet containing 200 mLs of hexane:acetone (1:1). Copper should not be exposed to air for long periods. Once all the Soxhlets were prepared the heating mantle was switched on and allowed to run at a steady pace (5 – 10 solvent exchanges per hour) for 3 days with overnight soaks. On the final day the Soxhlets were run for 2 hours and allowed to cool before being taken off the heating mantle.

After the Soxhlets had been allowed to cool for two hours the resultant extract solution was removed and then placed carefully into numbered turbovap vials and dried down using nitrogen to approximately 2 mL. The pressure did not exceed 7.5 psi and the temperature was set at 35 ^{o}C.

Alumina and silica were prepared by placing the correct weighed amount (13 g of alumina and 2 g of silica gel both 5% deactivated) into cleaned crucibles which were placed in the muffle furnace at 300 ^{o}C for 3 hours. Once 3 hours had elapsed the crucibles were allowed to cool to 200 ^{o}C before being covered with solvent washed tinfoil and placed on a metal tray in a desiccator to cool further. When cooled the alumina and silica were weighed into separate weighed flasks and a volume of water (5 % by weight) was added periodically while shaking the flasks. After all the water was added a final ten minute shake was completed to ensure an even distribution of water.

Glass columns were first washed with hexane before inserting ~ 2 g of 5 % deactivated silica gel followed by 13 g of 5 % deactivated alumina. The columns were then washed with 20 mL of hexane and the resulting eluant was discarded. The dried down samples were placed on top of the prepared column using a pipette and allowed to soak on to it. When the sample had soaked onto the top of the column, 200 mL of hexane was added and allowed to wash through the column before being collected at the bottom in a conical flask. Once all the solvent has been collected in the bottom flask it was transferred to washed turbo-vap vials, placed back in turbo-vap (7.5 psi and 35^{o}C) dried down to ~ 20 mL before 10 mL of isooctane was added and drying continued to ~ 1 mL.

3.4.1.2 Quality control

This extraction procedure was initially tested using QUASIMEME materials from previous rounds which had been already analysed and for which results, for PAHs and PCB/OCs were known. QUASIMEME material QPH062MS – PAHs/PCB and OCs in sediment, was tested. This initial testing provided good results in relation to Z score (Calculation shown appendix A.5) and subsequently further testing was undertaken to determine if this method could be used to analyse various QUASIMEME sediment sample types and ultimately if the method could be used to submit data to the QUASIMEME proficiency testing scheme. For further analysis of PAH and PCB/OCs in sediment more recent materials were chosen (QPH073MS, QPH074MS, QOR110MS and QOR111MS) and were extracted for PAH and PCB/OC analysis. Results for these extracted and analysed samples are shown below in *Table 3.9.* Generation of QUASIMEME Z scores are outlined in appendix A.5.

Table 3.9 Average results (n = 4) and assigned values of QUASIMEME sediment extracts (ng/g d w) for samples QPH073-74MS and QO110-111MS from Round 68 with calculated Z scores.

Compound ng/g	QPH073MS	Assigned (Z score)	QPH074MS	Assigned (Z score)
Acenaphthylene	1.02	1.82 (-2.44)	4.54	9.15 (-3.70)
Acenaphthene	1.81	1.57 (0.98)	86.9	128 (-2.57)
Fluorene	2.72	3.37 (-1.38)	159	213 (-2.03)
Phenanthrene	17.4	29.2 (-3.01)	1,258	1,466 (-1.14)
Anthracene	3.17	6.04 (-3.57)	243	342 (-2.31)
Fluoranthene	31.1	36.3 (-1.11)	1,787	1,575 (1.08)
Pyrene	22.6	25.7 (-0.46)	1,463	1,191 (1.83)
Chrysene	14.8	18.7 (-1.62)	565	425 (2.64)
Benzo(a)anthracene	13.3	16.2 (-1.38)	427	515 (-1.37)
Benzo(b)fluoranthene	17.2	29.3 (-3.09)	369	341 (0.65)
Benzo(k)fluoranthene	8.12	12.2 (-2.59)	258	177 (3.68)
Benzo(a)pyrene	13.7	15.0 (-0.66)	436	332 (2.50)
Indeno(1,2,3-cd)pyrene	13.3	20.4 (-2.69)	220	210 (0.38)
Dibenzo(a,h)anthracene			42.5	50.2 (-1.22)
Benzo(g,h,i)perylene	11.5	19.3 (-3.05)	181	196 (-0.60)
Compound ng/g	**QOR110MS**	**Assigned (Z score)**	**QOR111MS**	**Assigned (Z score)**
pp-DDE	0.12	0.12 (-0.12)	0.14	0.23 (-2.11)
PCB 31	0.22	0.25 (-0.60)	0.23	0.31 (-1.60)
PCB 28	0.29	0.33 (-0.71)	0.29	0.44 (-2.28)
HCB	0.08	0.14 (-2.10)	0.09	0.16 (-2.17)
PCB 52	0.24	0.26 (-0.47)	0.29	0.51 (-2.86)
PCB 118	0.42	0.37 (0.86)	0.77	0.74 (0.32)
PCB 105	0.11	0.09 (0.74)	0.19	0.21 (-0.57)
PCB 101	0.61	0.65 (-0.43)	0.86	1.04 (-1.24)
PCB 138	1.51	1.35 (0.88)	2.41	2.34 (0.23)
PCB 153	1.28	1.61 (-1.56)	1.92	2.82 (-2.49)
PCB 156	0.20	0.18 (0.67)	0.28	0.28 (0.04)
PCB 180	2.36	1.42 (4.92)	3.71	2.36 (4.42)

3.4.1.3 Discussion of QUASIMEME Results

The results shown (*Table 3.9*) for the extraction of PAHs in sediment are good overall and can be broken down as follows: satisfactory for 15 out of 29 (-2 - Z - 2) with 8 being questionable (-3 - Z – 3) and 6 being regarded as unsatisfactory (>3). The values

presented here are based on averages (n=4) of replicate samples. Overall these results are good in nature indicating that the method described in section 3.4.1.1 based on US EPA method 3540C [148] is adequate to analyse PAHs and in sediment samples. Naphthalene has been excluded from the results as LOD and LOQ results from method validation indicated the presence of trace levels in the laboratory and when coupled with low recoveries for this volatile compound correct quantification proved troublesome. The PCB/OC results are in the main very good with PCB 180 being consistently out of specification. All other compounds extracted using the method were good overall indicating that this method could also be used to extract marine sediment for PCB and OCs.

Following the success of the extraction and analysis of these 4 QUASIMEME materials it was decided to attempt to participate in the next round of materials for which the levels of compounds would be unknown. Results are shown in the following section.

3.4.1.4 Submission of Results to the QUASIMEME Proficiency Testing Scheme

The final stage in the process of validating both the extraction method and the instrumental analysis process was completed with the submission of blind QUASIMEME results for round 70 (*Table 3.10*).

Table 3.10 Results (ng/g d w) and assigned values for QUASIMEME sediment samples analysed for PAHs (QPH075- 76MS) and PCB/OC (QOR112 – 113) with associated Z scores.

Compound ng/g	QPH075MS	Assigned (Z score)	QPH076MS	Assigned (Z score)
Acenaphthylene	3.16	4.22 (-1.70)	10.1	12.2 (-1.30)
Acenaphthene			87.1	113 (-1.80)
Fluorene	9.9	8.08 (1.70)	231	186 (2.00)
Phenanthrene	56.7	49.8 (1.10)	1,834	1,491 (1.80)
Anthracene	11.5	10.9 (0.40)	367	335 (0.80)
Fluoranthene	95.2	80.1 (1.50)	1,825	1,551 (1.40)
Pyrene	86.9	73.9 (1.40)	1,409	1,175 (1.60)
Benzo(a)anthracene	31.2	46.7 (-2.60)	530	520 (0.20)
Benzo(b)fluoranthene	121	100 (1.70)	379	324 (1.30)
Benzo(k)fluoranthene	48.9	47.7 (0.20)	190	178 (0.50)
Benzo(a)pyrene	86.3	67.3 (2.20)	413	332 (2.00)
Indeno(1,2,3-cd)pyrene	141	124 (1.10)	236	215 (0.80)
Dibenzo(a,h)anthracene	24.2	24.2 (2.10)	59.1	48.2 (1.80)
Benzo(g,h,i)perylene	121	115 (0.40)	197	188 (0.40)
Compound ng/g	**QOR112MS**	**Assigned (Z score)**	**QOR113MS**	**Assigned (Z score)**
PCB 31	0.54	0.81 (-2.40)	0.40	0.38 (0.40)
PCB 28	0.72	0.78 (-0.50)	0.34	0.42 (-1.10)
PCB 52	8.21	8.70 (-0.40)	0.51	0.51 (0.00)
PCB 101	26.5	25.9 (0.20)		
PCB 105	11.0	9.6 (1.10)		
PCB 118	24.1	24.6 (-0.20)		
PCB 138	37.2	35.3 (0.40)		
PCB 153	37.0	38.5 (-0.30)		
PCB 156	5.23	4.66 (1.00)	0.43	0.00 (3.10)
PCB 180	37.1	37.1 (1.00)		
pp-DDE	0.97	1.08 (-0.80)	0.26	0.23 (0.80)
HCB	0.19	0.25 (-1.40)	0.37	0.20 (4.80)
pp-DDD	1.54	1.43 (0.60)	0.18	0.14 (1.20)
pp-DDT	0.89	0.73 (0.10)		
b-HCH	0.05	0.03 (0.02)		
g-HCH	0.06	0.04 (0.02)	0.04	0.05 (-0.20)
trans-nonachlor	0.03	0.02 (0.02)		

The samples were extracted and analysed in line with the methods outlined in sections 3.4.1.1 with results shown above (*Table 3.10*).

3.4.1.5 Discussion of Unknown QUASIMEME Results

There were 52 individual parameters reported (*Table 3.10)* with 46 out of 52 deemed satisfactory (-2 - Z - 2) while 4 were considered questionable (-3 - Z – 3) with 2 deemed to be unsatisfactory (>3). With these results showing good Z scores overall, the method development and validation of the sediment extraction and analysis method was deemed adequate and completed.

3.4.2 Method Development for Biota

The extraction method for biota used in this thesis is based on the Smedes and Askland method [149] which is used primarily to extract lipid from fish species and to determine gravimetrically the lipid percentage present. Once the lipid has been extracted it is cleaned up using column chromatography before being analysed. The flow chart shown below (*Fig 3.6*) gives an overall view of the process.

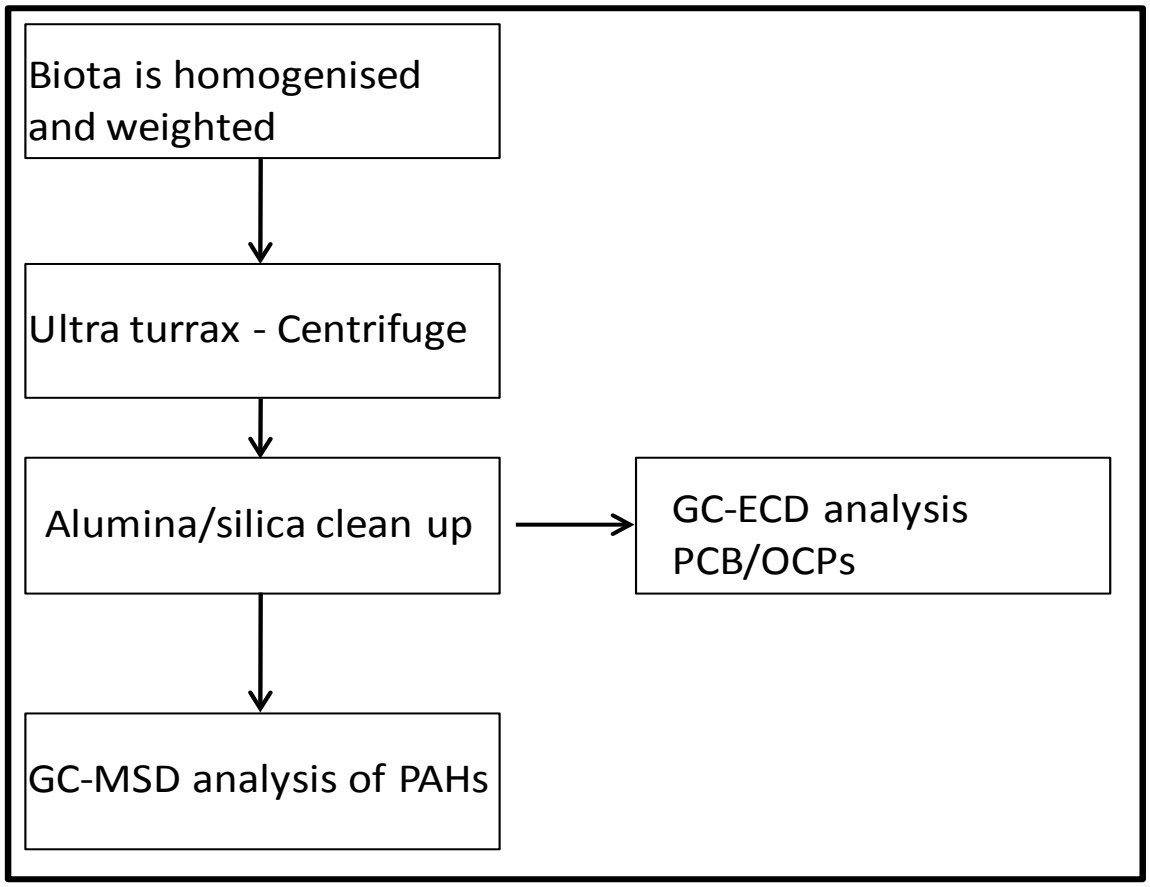


Figure 3.6 Flow chart showing the procedure used for the extraction and analysis of biota used for all analysis.

Biota which was collected during this project was sub-sampled at the MI laboratories. This involved removing a section of lipid from between the pectoral and dorsal fin of all animals. This sample was then homogenised before extraction using the method developed be Smedes and Askland [149] and analysis using the GC-ECD and GC-MS with further details shown in the following sections.

3.4.2.1 Extraction of Biota

All glassware and associated items are solvent washed before the extraction occurred. Biota samples are removed from the freezer (-28^{o}C) and allowed to thaw before being weighed into a centrifuge tube. The samples then had the same internal standards used to prepare the calibration standards added to them. Subsequently 16 mL of isopropanol and 20 mL of cyclohexane were added to the sample before it was homogenised using

an ultra turrax for a period of two minutes. After two minutes had elapsed 18 mL of deionised water was added and the ultra turrax was turned on for a further minute. Sodium chloride (~ 0.1 g) was added to the sample to prevent the formation of an emulsion before the sample was then placed in a centrifuge for 10 minutes at 2500 rpm. The less dense organic upper phase of the sample was then removed before 20 mL of a 13 % isopropanol/cyclohexane (w/w) mixture was added to the original flesh sample which was then homogenised for a further minute. Subsequently the sample was placed back in the centrifuge for a further 10 minutes at 2500 rpm before the upper layer was again removed. The two extracts where then combined in a pre-weighed turbo-vap vial before being dried down to remove all traces of solvent.

The samples were then carefully weighed to determine the lipid percentage before a known amount of hexane was added to them. Columns were prepared in a similar manner to section 3.4.1.1. The column was prepared using 2 g of 5 % de-activated silica and 6 g of 5 % deactivated alumina and 0.5 g of sodium sulphate. The sample was added to the column and washed through with 60 mL of hexane before being collected in a fresh pre-weighed turbo-vap vial. The resulting eluant is then dried down to approximately 20 mLs before having 10 mLs of iso-octane added and further dried to approximately 2 mLs.

3.4.2.2 Quality Control

To complete the method development and validation of this method for the determination of organic contaminants in biota it was again decided to use QUASIMEME reference materials. QUASIMEME samples from a previous round were used to estimate the overall success of this extraction method. A range of different matrices were chosen for validation. These included QBC024BT, QOR099BT and

QOR096BT – mussel tissue, QOR107BT – roach, QOR108BT which is a fish liver oil sample. *Table 3.11* and *Table 3.12* below shows the results of the initial Biota extraction and analysis using the methods set out in sections 3.4.2.1.

Table 3.11 Average (n =9) concentrations (ng/g w w) and assigned values (average Z scores in parenthesis) of BFRs resulting from the extraction and analysis of QUASIMEME biota samples (QBC024BT) using the procedures outlined in section 3.4.2.1

Compound ng/g	Average Value	Assigned Value (Z Score)
BDE 28	0.031	0.03 (0.80)
BDE 47	0.267	0.27 (0.02)
BDE 100	0.211	0.07 (12.7)
BDE 99	0.088	0.09 (0.00)
BDE 154	0.020	0.03 (-0.63)
BDE 153	0.015	0.01 (1.22)

The results in *Table 3.11* above show that average repeated analysis of BFR compounds in the QUASIMEME reference material generates good results for all compounds apart from BDE 100 where the estimated value is far above the assigned (0.07 ng/g). Further analysis using different materials need to be completed for BDE 100 to ensure complete confidence in the analysis of BFRs.

Table 3.12 Concentrations (ng/g w w) and assigned values (Z scores in parenthesis) of PCB/OCs resulting from the extraction and analysis of QUASIMEME biota samples (QOR099, 107 and 108BT) using the procedures outlined in sections 3.4.2.1.

Compound ng/g	QOR099BT	Assigned (Z score)	QOR107BT	Assigned (Z score)	QOR108BT	Assigned (Z score)
PCB 31	0.19	0.19 (0.00)	2.01	2.06 (-0.19)	3.99	3.78 (0.43)
PCB 28	0.24	0.23 (0.24)	3.74	3.76 (-0.04)	10.6	10.5 (0.08)
PCB 52	0.59	0.60 (-0.11)	18.5	18.7 (-0.08)	23.2	23.7 (-0.18)
PCB 101	2.64	2.57 (0.21)	51.8	51.4 (0.07)	62.9	63.7 (-0.10)
PCB 118	1.92	1.98 (-0.23)	26.6	27.1 (-0.16)	69.8	69.9 (-0.02)
PCB 153	7.47	7.56 (-0.09)	101	105 (-0.28)	189	219 (-1.10)
PCB 105	0.39	0.39 (0.00)	4.39	4.49 (-0.17)	16.5	16.3 (0.10)
PCB 138	4.31	4.21 (0.19)	53.4	53.3 (0.01)	133	132 (0.05)
PCB 156	0.15	0.17 (-0.59)	2.84	2.95 (-0.29)	8.02	8.41 (-0.37)
PCB 180	0.39	0.45 (-0.87)	16.8	19.4 (-1.06)	45.0	45.5 (-0.09)
HCB	0.10	0.10 (0.00)	3.73	3.74 (0.00)	14.7	14.0 (0.00)
pp-DDE	1.19	1.20 (-0.10)	16.0	16.0 (0.00)	86.4	83.1 (0.30)
pp-DDD	0.31	0.37 (-1.02)	2.49	3.58 (-2.38)	14.8	26.7 (-3.55)
Dieldrin	0.88	0.84 (0.34)	0.59	0.61 (-0.23)	35.8	36.7 (-0.19)
trans -nonaclor	0.26	0.11 (5.63)	0.26	0.22 (1.00)	7.85	7.43 (0.45)
a-HCH	0.01	0.02 (-0.75)	0.05	0.06 (-0.59)	1.33	1.37 (-0.22)
g-HCH	0.03	0.04 (-0.52)	0.09	0.07 (0.94)		
HCBD					1.46	1.41 (0.26)

The Smedes and Askland method [149] can be considered acceptable for the extraction and analysis of PCBs and OCs in biota as the results in *Table 3.11* and *Table 3.12* show. PAHs in general are found in low levels in fish but are readily accumulated in mussel tissues. To validate the extraction methodology and quantification procedure used in relation to PAHs, two mussel tissues (QOR096 -099BT) were also extracted using the extraction method set out in section 3.4.2.1. The results are shown in the table below (*Table 3.13).*

Table 3.13 Concentrations (ng/g w w) and Z scores of PAHs resulting from the extraction and analysis of QUASIMEME biota samples (QOR096 – 99BT) using the procedures outlined in sections 3.4.2.1

Compound ng/g	QOR099BT	assigned	Z score	QOR096BT	assigned	Z score
Acenaphthylene				0.42	0.42	0.0
Acenaphthene	1.01	0.99	0.1	0.25	0.31	-0.5
Fluorene	2.18	1.62	1.9	0.70	0.69	0.1
Phenanthrene	13.89	11.10	1.9	5.59	5.66	-0.1
Anthracene	0.98	1.01	-0.1	0.21	0.24	-0.3
Fluoranthene	15.64	16.70	-0.5	2.49	2.42	0.2
Pyrene	12.79	13.20	-0.2	2.88	2.04	2.4
Chrysene	7.42	7.45	0.0	1.14	1.09	0.2
Benzo(a)anthracene	5.49	5.45	0.0	0.93	0.92	0.1
Benzo(b)fluoranthene	7.13	7.28	-0.2	1.19	0.67	2.8
Benzo(k)fluoranthene	2.82	2.90	-0.2	0.53	0.21	2.6
Benzo(a)pyrene	3.31	3.08	0.5	0.17	0.13	0.4
Indeno(1,2,3-c,d)pyrene	2.55	3.00	-0.9	0.49	0.13	3.0
Benzo(g,h,i)perylene	3.42	3.60	-0.3	0.67	0.38	1.9
Dibenzo(a,h)anthracene	0.61	0.82	-1.4			

3.4.2.3 Discussion of QUASIMEME Biota Results

The results for the extraction of QUASIMEME materials (QOR099, 107 and 108BT) for PCBs and OCPs shown above (*Table 3.12*) are good with 36 of the results showing a satisfactory Z score (-2 - Z - 2). This indicates that the Smedes and Askland method [149] is adequate for this type of analysis. The resultant Z scores shown (*Table 3.13*) for the extraction of QUASIMEME materials (QOR096 and 99BT) for PAHs are also good with 24 out of the 28 reported showing satisfactory Z score (-2 - Z - 2) while 4 show a questionable Z score (-3 - Z – 3) and there are no unsatisfactory results (>3). Following the success of the extraction and analysis of these 5 QUASIMEME materials it was decided to participate in the next round of materials for which the levels of compounds would be unknown. Results are shown in the following sections.

3.4.2.4 Submission of Results to QUASIMEME Proficiency Testing Scheme

Again the final stage of method development and validation was the submission of unknown concentrations estimated in materials for round 70 of the QUASIMEME proficiency testing scheme.

Table 3.14 Resulting concentrations (ng/g w w) and assigned values (Z scores in parenthesis) of PCB, PAH and OCs from QUASIMEME round 70 materials extracted using the methodologies described in section 3.4.2.1.

Compound ng/g	QOR112BT	Assigned (Z score)	QOR113BT	Assigned (Z score)
PCB 31	0.26	0.19 (2.10)	4.13	4.44 (-0.50)
PCB 28	0.34	0.23 (2.40)	8.68	8.51 (0.20)
PCB 52	1.01	0.91 (0.80)	43.6	44.2 (-0.10)
PCB 101	3.04	2.96 (0.20)	98.9	106 (-0.50)
PCB 105	0.39	0.51 (-1.50)	6.45	7.06 (-0.70)
PCB 118	2.38	2.30 (0.30)	8.12	7.33 (-0.10)
PCB 153	8.74	8.87 (-0.10)	33.7	31.0 (-0.50)
PCB 138	3.45	4.24 (-1.50)	94.7	111 (-1.20)
PCB 156	0.20	0.19 (0.40)	5.68	6.44 (-0.90)
PCB 180	0.42	0.38 (0.60)	6.89	7.63 (-1.80)
HCB	0.06	0.06 (-0.10)	3.35	5.66 (-3.20)
pp-DDE	1.23	1.29 (-0.30)	29.2	30.2 (-0.30)
pp-DDD	0.58	0.32 (5.00)	7.42	7.66 (-0.20)
a-HCH	0.03	0.02 (0.50)	0.04	0.06 (-0.80)
g-HCH	0.05	0.04 (0.80)	0.08	0.05 (1.60)
trans-nonachlor	0.10	0.06 (2.20)	0.48	0.48 (0.00)
Compound ng/g	**QPH067BT**	**Assigned (Z score)**	**QPH068BT**	**Assigned (Z score)**
Acenaphthylene	0.49	0.36 (0.90)	9.42	10.5 (-0.80)
Acenaphthene	0.76	0.70 (0.30)	8.51	7.97 (0.50)
Fluorene	1.33	1.10 (1.00)	2.02	1.50 (1.80)
Phenanthrene	7.70	8.13 (-0.40)	3.20	3.19 (0.00)
Anthracene	0.68	0.68 (0.19)	0.63	0.73 (-0.50)
Fluoranthene	13.4	13.4 (0.00)	2.72	3.03 (-0.60)
Pyrene	14.9	11.2 (2.40)	2.37	2.60 (-0.60)
Chrysene	4.64	4.85 (-0.30)	1.20	1.30 (-0.40)
Benzo(a)anthracene	4.75	4.88 (-0.20)	1.11	1.06 (0.20)
Benzo(b)fluoranthene	3.98	4.61 (-0.90)	1.00	1.02 (-0.10)
Benzo(k)fluoranthene	1.76	1.94 (-0.50)	0.41	0.39 (0.10)
Benzo(a)pyrene	1.32	1.41 (-0.30)	1.12	0.95 (0.80)
Indeno(1,2,3-cd)pyrene	1.43	1.59 (-0.50)	3.49	3.91 (-0.70)
Dibenzo(a,h)anthracene	0.35	0.35 (0.00)	1.55	
Benzo(g,h,i)perylene	2.19	2.27 (-0.20)	2.01	1.93 (0.20)

These materials included two chlorinated organics (PCBs/OCs) in biota (QOR112 – 113BT) and 2 PAH in biota materials (QPH067 – 068BT). There was no submission material dispatched for BFRs in biota for round 70 of the QUASIMEME proficiency testing scheme. The samples were extracted and analysed in accordance with the methods set out in section 3.4.2.1 with the resulting data shown below in *Table 3.14.*

3.4.2.5 Discussion of Results of Unknown QUASIMEME Results

There were 61 individual results reported to the QUASIMEME proficiency testing scheme following the extraction and analysis of the 4 materials provided (QOR112 and 113BT, QPH067 and 068BT) for round 70. Of these results reported (*Table 3.14*) 55 obtained a satisfactory Z score (-2 - Z - 2) while only 4 had questionable Z score (-3 - Z - 3) results associated with them. There were 2 unsatisfactory (>3) results in this case. Overall this method was deemed satisfactory and was used to analyse biota reported in this study.

3.5 Passive Sampling Devices

The suitability of PSDs to estimate dissolved water concentrations of POPs and as a tool to satisfy legislative requirements (WFD, OSPAR) depends on a number of parameters which relate to the quality control of the data generated. The availability and quality of *Log* K_{pw} partition coefficients and sampling rate models should be sufficiently accurate.[147] Initially an evaluation of the concentrations of compounds found in solvent blanks, preparation and field controls should allow an accurate estimation of a limit of detection for each compound found in deployed samplers. The effect of uncertainties in K_{pw} and subsequently on R_s values on the final C_w values should also be assessed. Further information on the quality control of data generated during this study is shown

in the following sections. Preparation, spiking and deployment aspects of PDMS PSDs are further detailed in appendix A.6. The information related to analysis of PDMS passive samplers does not relate to the use of SPMDs which are further discussed in chapter 5.

3.5.1 Extraction of PDMS Passive Samplers

Passive sampler jars were removed from the freezer and allowed to defrost at -4 ^{o}C. The passive sampler sheets were first patted dry to remove any excess water before all six membranes being placed carefully in Soxhlet extraction units. Preparation and field controls were treated in the same manner as the actual sample PDMS sheets. 200 mL of methanol/acetonitrile (1:2 v/v) was used to extract the sheets for 10 hours. A procedural blank and a recovery blank were treated in the same manner. Once the extraction period was over the sheets were removed and allowed to dry for a short period before being again dabbed dry with tissue and weighed to 3 decimal places. This weight constitutes ***m*** or mass of the samplers which is important in working out the sampling rate (R_s) and dissolved water concentration (C_w).

The solvent was removed from the apparatus once cooled, and dried down using a water bath to ~2 mL before being placed on a pre-rinsed glass column with 500 mgs of silica gel (prewashed with 10 mL of methanol/acetonitrile 1:2 v/v) and eluted with 10 mL of the methanol/acetonitrile mixture used above. The eluant was then collected before having 100 mL of hexane added along with some anti-bumping granules and boiled on a water bath (85 ^{o}C) until ~10 mL remained. 20 mL of 2,2,4-trimethylpentane was then added and the sample again dried to ~2 mL using a turbo-vap. The samples then had relevant internal standards added before analysis (section 3.3.1).

3.5.2 Quality control

Quality control for passive samplers begins with assessing the concentrations of contaminants found in the field control and preparation controls and the calculation of the LOD for each compound to ensure that the levels of compounds with values close to the LOD are critically assessed. Final C_w concentrations (ng/L) can be compared to mussel concentrations to ensure that there was no over or under estimation of the levels present at a particular site. Replicate samplers can be deployed in tandem to ensure further quality of the passive sampler derived C_w concentrations with final quality assurance satisfied by taking part in a proficiency testing scheme, in this case the network of monitoring and related organisations for monitoring and bio-monitoring of emerging environmental pollutants (NORMAN). Information relating to these parameters, among others is shown in the following sections.

3.5.2.1 Accuracy of K_{pw}

The accuracy of passive sampler-water partition coefficients (K_{pw}) can often be difficult to assess in that data in the literature can often relate to single, or small numbers of studies on a particular type of sampler which may have low uncertainty errors based on replicates from one experiment. Where inter-laboratory variability data is available more realistic error estimates can be made.[147] In the case of PDMS silicone rubber passive samplers it has been found that K_{pw} values for PAHs and PCBs from different studies can vary by up to 0.55 log units.[146] The accuracy of K_{pw} values is important only for those compounds that reach equilibrium with the surrounding medium and irrelevant for those in the linear uptake phase. However the estimate of C_w values depends on the accuracy of R_s values which depend directly on accurate estimation of K_{pw} values for

PRCs. In this study *Log* K_{pw} values (appendix A.1) for all compounds used are based on the work of Smedes *et al.* [146,14] which are calculated using the co-solvent method.

Non co-solvent estimation of K_{pw} values are determined following equilibrium of the material and water phase containing the compounds of interest followed by extraction and analysis of both phases. The main difficulties with this method are improper estimations of low levels found in the water phase caused by sorption of compounds to the walls of the container or to suspended particulate matter present. Smedes *et al.* [146] report that the co-solvent method, where partition coefficients are measured in a range of methanol-water mixes and pure water, stabilises the solutions and increases the solubility of compounds in the aqueous phase. The resulting concentrations are now above the limit of detection coupled with the cancelling out effect of the co-solvent method on the particulate matter present allows a more accurate partition coefficient estimation to be made. Lohmann *et al.* [147] report that the primary source of error in these estimations is the use of pure water K_{sw} values. The use and validation of co-solvent models improves the accuracy of K_{pw} values and suggests that residual uncertainty of the measured values is no longer a dominating factor in the overall uncertainty of passive sampling.[146]

3.5.2.2 Accuracy of R_s

The accuracy of the sampling rate estimation is dependent on a number of factors including the quality of the K_{pw} values but also the quality of the modelling used to estimate R_s. Lohmann *et al.* [147] report that sampling rates are limited by diffusion into the sampler (membrane controlled) for compounds with low Log K_{ow} values (<3) and by transport through the water boundary layer (WBL controlled) for compounds with higher Log K_{ow} values. Modelling of WBL controlled accumulation into passive

samplers is straightforward as hydrodynamic theory states that sampling rates are proportional to the aqueous diffusion coefficient to the power of 2/3 which leaves only the proportionality constant to be estimated using the data generated by PRCs.[147] Semi-empirical correlations with molar volume, or in this study molar mass, are used to derive values for diffusion coefficients which, depending on the diffusion model used, show R_s to be proportional to $M^{-0.47}$.[103]

Because hydrophobicity and molecular size are correlated for non-polar compounds and R_s can be related to hydrophobicity a weak decrease in R_s with increasing K_{ow} can be expected. Rusina *et al.* [150] report that R_s is proportional to $K_{pw}^{-0.08}$ and $K_{ow}^{-0.08}$. This indicates that the *Log* R_s – *Log* K_{pw} relation is linear and that uptake is controlled by the WBL for compounds with a Log K_{ow} value of 3 – 7.

In the case of those compounds whose uptake is membrane controlled the modelling used can be complex in that the sampling rate decreases with time. In addition diffusion coefficients for the compounds must be available. A practical but approximate solution suggested by Booij *et al.* [111] is to establish an empirical correlation between membrane controlled sampling rates and Log K_{ow} at different temperatures. Membrane controlled accumulation by passive samplers can be considered in exceptional circumstances where the deployment time is short or the sampling rate is very high.

Booij *et al.* [119] suggest that the quality of the estimation of R_s can be improved by using the un-weighted nonlinear least squares (NLS) method where all PRC data can be used, including where PRC concentration remaining is close to the LOD or where PRCs are non-depleted. This approach improves R_s estimation and means that uncertainties can always be modelled using PRC data. Efforts to reduce bias and variability should

concentrate on uncertainties in K_{pw} estimation, this can be improved by increasing the number of PRCs used to calculate R_s. The use of the unweighted NLS method is described in more detail in chapter 4 (4.4.2).

3.5.2.3 Detection Limits

Detection limits for PSDs are also an important aspect of quality control. It is important that the LOD be assessed using the concentration of contaminants found in field and preparation of blanks. The field controls can yield information on the analyte uptake that occurred during transport, deployment and subsequent retrieval of passive samplers while the preparation blanks can yield information on the levels of contamination that can take place during the extraction and analysis of samplers. In this study LOD was calculated using the average blank values calculated in all field control and preparation blanks multiplied by three. Any calculated value (ng/sampler) which was lower than the LOD value calculated then had the C_w concentration calculated using the LOD value and reported as a less than value.

3.5.2.4 PSD/ Mussels Inter-comparison

Smedes *et al.* [89] report that passive sampling derived C_w concentrations of contaminants act as an indicator of the contaminant levels in the environment and that concentrations of POPs found in mussels (C_m) in the same area are thought to be related to the C_w concentrations. This relationship between C_w and C_m is represented by the bio-accumulation factor (BAF). The BAF is a ratio between C_w and C_m values and is analogous to *Log* K_{pw}. Passive sampler water partition coefficients, like Log K_{ow} are thermodynamic properties and have constant values however the BAF can be species dependent and can change due to environmental impacts on the mussels such as growth,

reproductive status and the availability of food. Temporal and spatial factors can also play a role.

The uptake and partition process in passive samplers is similar to that of mussels. The different chemical properties of POPs allow accumulation with the sampler or mussel and over time equilibrium will be reached. Examination of the BAF between mussels and passive samplers can therefore be used as a proxy indicator of the dissolved water concentrations present in the sampled medium and thus can contribute to quality control aspects for passive samplers.

The collated uptake of passive samplers (and especially PDMS) relative to mussels has been well documented.[123,89] Further to these studies a "proof of concept" study was completed at one test site (Kilkieran in Co. Galway – Chapter 6) during this study where mussels from the test location were analysed in parallel to the deployed PDMS. Bioaccumulation factor (BAF) models were then calculated and results compared to previous literature studies namely those completed by Geyer *et al.*, [27] Smedes [124] and Thorsen *et al.*[151]

Two BAF models were constructed using mussel POP concentrations (dry weight and dry weight lipid normalised ng/kg) divided by PDMS derived water concentrations (ng/L) at the Kilkieran site. Data were available for a number of PCBs, PAHs, OCs and PBDEs. In total data from 34 POPs measurable in both compartments were available for the construction of the BAF models. It should be noted that this site is considered to be relatively unimpacted therefore low contaminant levels were determined for a number of parameters. Where data were reported as <values or were not detected these were

omitted from the model. Log BAFs were then plotted against the appropriate *Log* K_{pw} for each parameter.

A number of BAF regression equations are available from the literature for primarily PAHs and a combination of PAH/PCBs as modelled by,

Log BCF = 0.749 (Log K_{ow}) − 1.06 : Thorsen (PAH only)

Log BCF_L = 0.96 (Log K_{ow}) + 0.22 : Geyer (PAH/PCBs)

Log BCF = 0.82 (Log K_{ow}) – 0.52 : Smedes (PAH/PCBs)

Log $BAF_{d\,w}$ = 0.80 (*Log* K_{pw}) + 0.13 : This study (PAH, OCs, PCBs and PBDEs)

Log BAF_L = 0.80 (*Log* K_{pw}) + 1.79 : This study (PAH, OCs, PCBs and PBDEs)

The model generated by Geyer *et al.* [27] is based on lipid (BCF_L), however the basis of the model generated by Thorsen *et al.* [151] is unclear. This relationship is further illustrated in *Fig 3.7* and *3.8*.

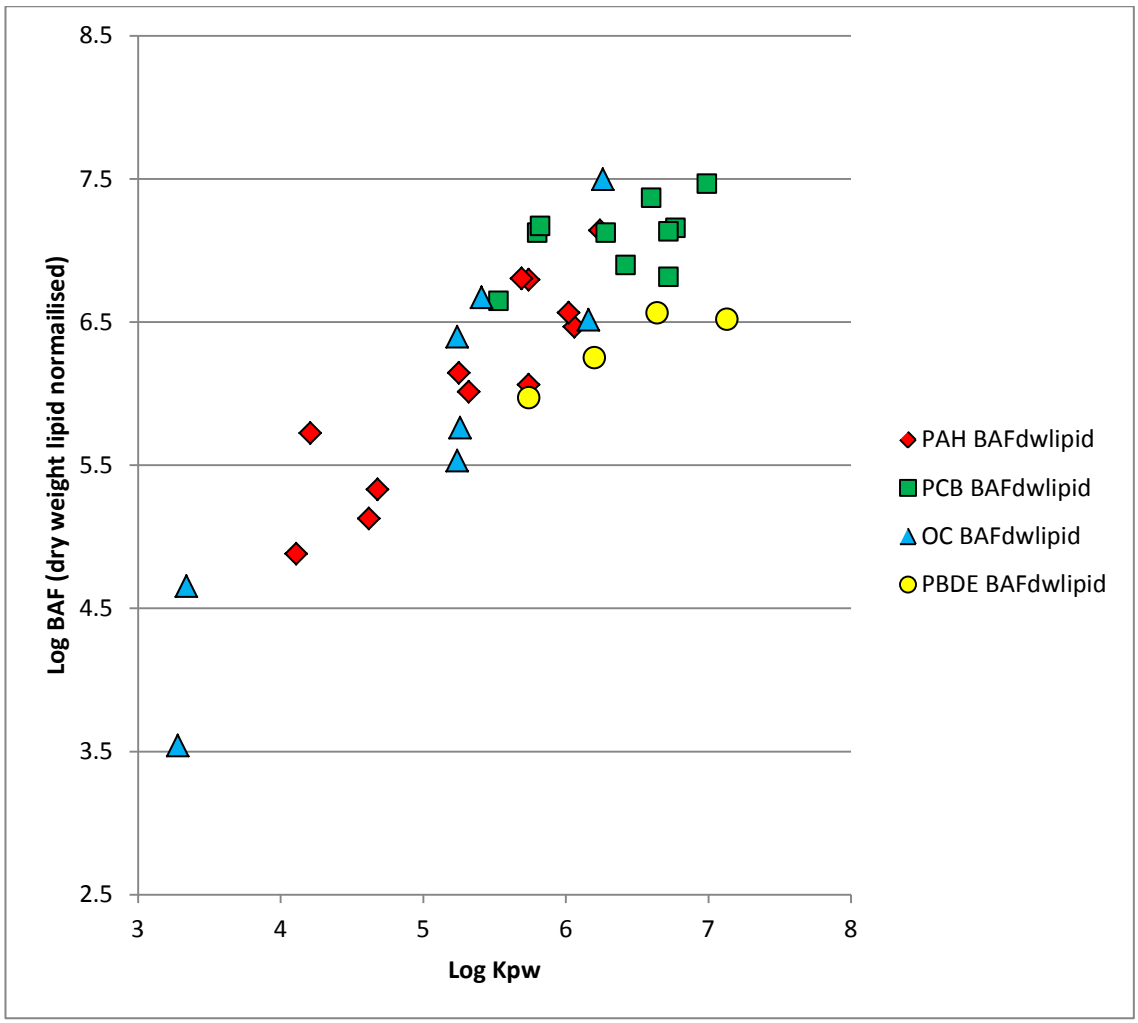


Figure 3.7: Relationship between BAFs (dry weight lipid normalised basis) calculated from the Kilkieran test site and parameter *Log* K_{pw}. Relationship equation: Log BAF_L **= 0.80 (*Log* K_{pw}) + 1.79** r^2 **= 0.75.**

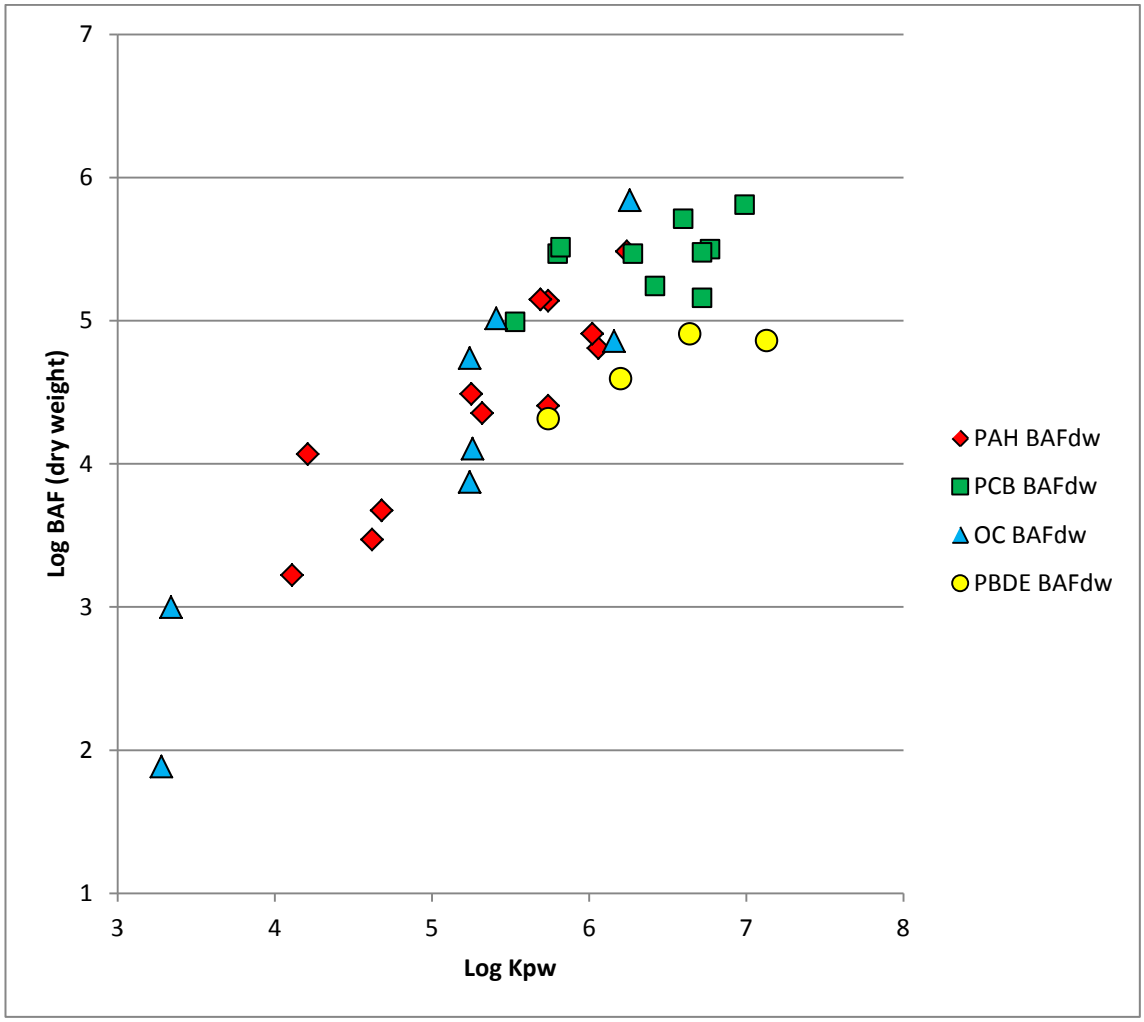


Figure 3.8: Relationship between BAFs (dry weight) calculated from the Kilkieran test site and parameter *Log* K_{pw}. Relationship equation: Log $BAF_{d\,w}$ = 0.80 (*Log* K_{pw}) + 0.13 r^2= 0.75.

Overall the slopes for the lipid normalised equations derived during this study are similar to those from previous research and especially in relation to those derived by Smedes in the PSTS.[118] It should be noted that where the *Log* K_{pw} was lower than approximately 3.4 and/or greater than 7.0 that the relationship deteriorated to a greater extent. This study documents for the first time the inclusion of PBDEs in addition to other pollutants in the generation of passive sampling derived BAFs. It can be concluded that the use of mussel tissue concentrations in combination with PS derived water concentration data can be a powerful tool in the prediction of water

concentrations especially where POP *Log* K_{pw} ranges lie between 3.4 to <7.0. As such this study provides evidence supporting the applicability of PDMS passive samplers in the field for the determination of the range hydrophobic POPs completed during this thesis.

3.5.2.5 Reproducibility of PSD Results

Another aspect of quality control as it relates to the use of passive samplers is the comparison of reproducibility between samplers at the same site. During this study simultaneous deployments at a single location took place only at Cork (Chapter 6) and this relates to a dual deployment at one site. The results for the two Cork samplers are shown in *Table 3.15* below with further details on the deployment shown in chapter 6.

Table 3.15 Comparison of upper-bound C_w concentrations (ng/L) estimated for replicate PSDs deployed at Cork harbour.

Compound ng/L	Cork 1	Cork 2	Compound ng/L	Cork 1	Cork 2
Acenaphthylene	1.11	0.85	PCB 44	0.01	0.01
Acenaphthene	2.02	1.37	PCB 101	0.02	0.02
Flourene	5.32	3.90	PCB 149	0.10	0.11
Phenanthrene	9.48	8.67	PCB 118	0.15	0.12
anthracene	0.48	0.63	PCB 153	0.14	0.15
Flouranthene	5.60	4.98	PCB 138	0.15	0.14
Pyrene	3.39	3.07	PCB 156	0.07	0.14
Chrysene	0.47	0.41	PCB 180	0.12	0.12
Benzo(a)anthracene	1.17	1.06	PCB 170	0.02	0.04
Benzo(b)flouranthene	0.76	0.67	PCB 194	0.01	n.a
Benzo(k)flouranthene	0.76	0.64	PCB 209	0.01	0.01
Benzo(a)pyrene	0.28	0.22			
Indeno(1,2,3-cd)pyrene	0.47	0.31	∑PCB	0.80	1.04
Dibenzo(a,h)anthracene	0.11	0.05			
Benzo(g,h,i)perylene	0.39	0.27	HCB	0.08	0.08
			pp-DDE	0.08	0.09
P/A	19.7	13.7	op-DDD	3.22	3.01
Fl/Py	1.65	1.62	op-DDT	0.02	0.02
∑LPAHs/HPAHs	1.38	1.32	ppDDD	5.99	6.18
∑PAH	31.8	27.1	pp-DDT	0.02	0.02
Stat test result					
Student T	0.01		∑OC	12.0	12.0
Critical value	2.04				

n.a – not analysed

The two samplers deployed in Cork harbour were deployed on the same passive sampler cage meaning that the samplers were deployed for the same time period in the same location. Results shown in *Table 3.15* indicate that samplers deployed in this manner can be used to confer a degree of quality assurance to the sampler results in that the concentrations illustrated are very similar in nature. The ∑PAHs from the two samplers differ only slightly from each other with the first replicate estimation of 31.8 ng/L while the second replicate was 27.1 ng/L. ∑PCBs were also similar with the first replicate at 0.80 ng/L and the second at 1.04 ng/L while the ∑OCs also compared well also, 12 and 12 ng/L for the first and second replicates. A students t Test ($\alpha = 0.05$, critical value =

2.04, 95 % confidence interval) was completed on the differences between data in *Table 3.15*, with the result of 0.01 indicating the data sets are not significantly different.

The sampling rates calculated from the retained PRC fractions for both samplers at the one site also showed a very similar result (9.09 and 9.02 L/d, chapter 6) which is to be expected since they used the same method for R_s calculation as well as the same K_{pw} values. However the fact that both samplers did give similar results confers a degree of quality assurance to the results.

3.5.2.6 Norman Inter-calibration Exercise

To give the passive sampling data generated throughout this thesis an element of quality control and assurance it was decided to participate in a passive sampler inter-calibration exercise organised by the network of monitoring and related organisations for monitoring and bio-monitoring of emerging environmental pollutants (NORMAN). This project was designed to give environmental managers an insight into the quality of data that can be produced by passive samplers and to provide some element of quality control to the European Commission in relation to the use of PSDs to satisfy WFD parameters relating to hazardous chemicals in water. The study itself asked participants to:

- Provide samplers of their own design which were exposed at references site by the organisers,
- Analyse a sampler provided by the organisers,
- Analyse a standard solution provided by the organisers.

This study was supported by the provision and analysis of a set of PDMS passive samplers as used in the NORMAN calibration exercise and which were analysed for

brominated flame retardants (BFRs) in according with method guidelines set out in section 3.5.1. Results on a ng/sampler basis are shown in *Table 3.1*6. BFRs is a term given to a series of polybrominated di-phenyl ethers (PBDEs). The NORMAN study concentrated on these compounds as well as some pesticides, steroid hormones, fluorinated surfactants and bisphenol A/triclosan. Results shown below (*Table 3.16*) are average values based on the extraction of 4 sets of 3 sheets and are in close agreement

Table 3.16 Average concentrations (N = 4) (ng/sampler) calculated by the MI laboratories along with those provided by the central organising laboratory.

Compound	MI Values		Organiser values	
(ng/sampler)	Average	STDEV	Average	STDEV
PBDE 28	1.2	0.1	1.04	0.6
PBDE 47	23.1	2.8	19.01	2.7
PBDE 100	2.6	0.2	2.91	2
PBDE 99	9.6	1.2	9.5	1.8
PBDE 154	0.2	0.0	0.28	0.1
PBDE 153	0.2	0.0	0.24	0

with those provided by the central organising laboratory. Although dissolved water concentrations are not available the results presented in *Table 3.16* indicate that the extraction method employed during this study returns results in accordance with those of the NORMAN network regarding BFRs.

3.6 Conclusion

The instrumentation and method development for all matrices (PS, biota and sediment) provided individual and collective challenges that needed to be overcome. The extraction and analysis of biota and sediment had been a regular procedure at the MI where a change in instrumentation from GC-ECD to MS was the primary challenge. The final submission of QUASIMEME data for biota and sediment confers a degree of

quality control to the extraction and instrumentation validation for these matrices. Passive samplers provided a different challenge in that passive sampler extracts must be analysed with no reference materials with which to compare the method (apart from NORMAN for PBDE) and calculate final C_w concentrations. Initial extractions and analysis of passive samplers provided insights into the areas in which improvements could be made be it the extraction procedure at the MI laboratory or the instrumental analysis or finally the calculations of R_s and C_w which meant that the integrity of the data generated was always improving.

While there is currently no recognised PSD proficiency testing scheme a great deal of quality assurance can be conferred on the passive sampler data generated in this study. Replicate analysis of samplers deployed at the same location has also been shown to produce results which are similar. Analysis of the NORMAN inter-calibration study PSDs showed results in close agreement with assigned values. The methods applied to calculate R_s and C_w results are 'state of the art' and have been shown to address many of the problems associated with passive sampler derived dissolved water concentrations.[115]

With all of this information in mind and based on the evidence documented above with respect to method development and validation including the addition of rigorous quality control aspects (field controls and preparation controls, QC performance in proficiency studies for biota and sediment) and the inclusion of CRM data all methods are deemed to be fit for purpose. To illustrate this point *Table 3.17* below shows the type of quality control data generated during analysis of all environmental samples (sediment, biota and PSDs). The biota data in *Table 3.17* were generated using repeated measurements of a QUASIMEME sample (QOR099BT) (n = 17) which was used as a CRM for biota extractions as it contains certified levels of PCB, OC, PAH and BFRs. LOD and LOQ

measurements for the biota data are based on the instrumental LOD/LOQ data generated in appendix A.4 *Table 2* and the sample multiplier calculated during the lipid extraction.

For sediment shown in *Table 3.17* data for QUASIMEME round 70 was used as this was shown to be of high quality (section 3.4.1.4). Again LOD and LOQ data are calculated using the instrument LOD/LOQ with a sample weight applied to it. Accuracy is a measure of the percentage recovery between calculated and assigned QUASIMEME values for both sediment and biota. Precision is a measure of the percentage relative standard deviation between calculated and assigned QUASIMEME values.

Table 3.17 QC data generated for biota, sediment and passive samplers using repeated analysis of QOR099BT (n=17) for biota, round 70 QUASIMEME materials for sediment and NORMAN PSDs (pg/L) for passive samplers

	Accuracy	Precision	LOD	LOQ
Compound	**%**	**%RSD Range**	**pg/g**	**pg/g**
PAH				
Biota	70.3 -135	9.37 - 13.5	0.5 - 9.9	1.16 - 23
Sediment	66.8 - 128	0.41 - 13.4	0.39 - 3.51	0.91 - 8.20
PSD	N/A	N/A	1.04 - 26.1	N/A
PCB				
Biota	73.9 - 130	3.17 - 7.92	0.96 -5.62	2.24 - 10.7
Sediment	67 -115	0.24 - 13.4	0.75 - 1.32	1.75 - 3.07
PSD	N/A	N/A	0.67 - 18.4	N/A
OC				
Biota	75.0 - 165	11.4 - 38.5	0.52 - 9.48	0.62 - 22.1
Sediment	62.5 - 153	0.31 - .051	0.21 - 3.37	0.63 - 7.87
PSD	N/A	N/A	2.02 - 7.33	N/A
BFR				
Biota	66.7 - 138	8.37 - 14.8	1.07 - 18.0	2.5 - 45.9
Sediment	N/A	N/A	0.84 - 7.0	1.95 - 16.3
PSD	75.5 - 122	6.89 - 15.2	2.29 - 14.1	N/A

N/A – not applicable

For passive samplers the NORMAN inter-calibration data for PBDE (BFR) compounds was used to calculate accuracy and precision while the LOD value is calculated as described in section 3.5.2.3. Only LOD data is generated for the passive samplers as this is the concentration below which a stated value is indistinguishable from noise.

Chapter 4: The Application of Passive Samplers in Conjunction with Biological Tissue and Sediment analysis to Investigate Pollutant Loadings in the Burrishoole Catchment Area of Co. Mayo

4.1 General Introduction

Lough Feeagh is located in Co. Mayo near the town of Newport, situated on the west of Ireland close to the Atlantic coast and forms part of the Burrishoole catchment area which incorporates Lough Furnace and the surrounding rivers (*Fig 4.1*). It is strongly affected by the temperate oceanic climate prevalent in the region. Lough Feeagh is approximately 4 km^2 with a maximum depth of 45 m and an average depth of 14 m. As it is part of the Burrishoole catchment area it is therefore an important index for salmon.

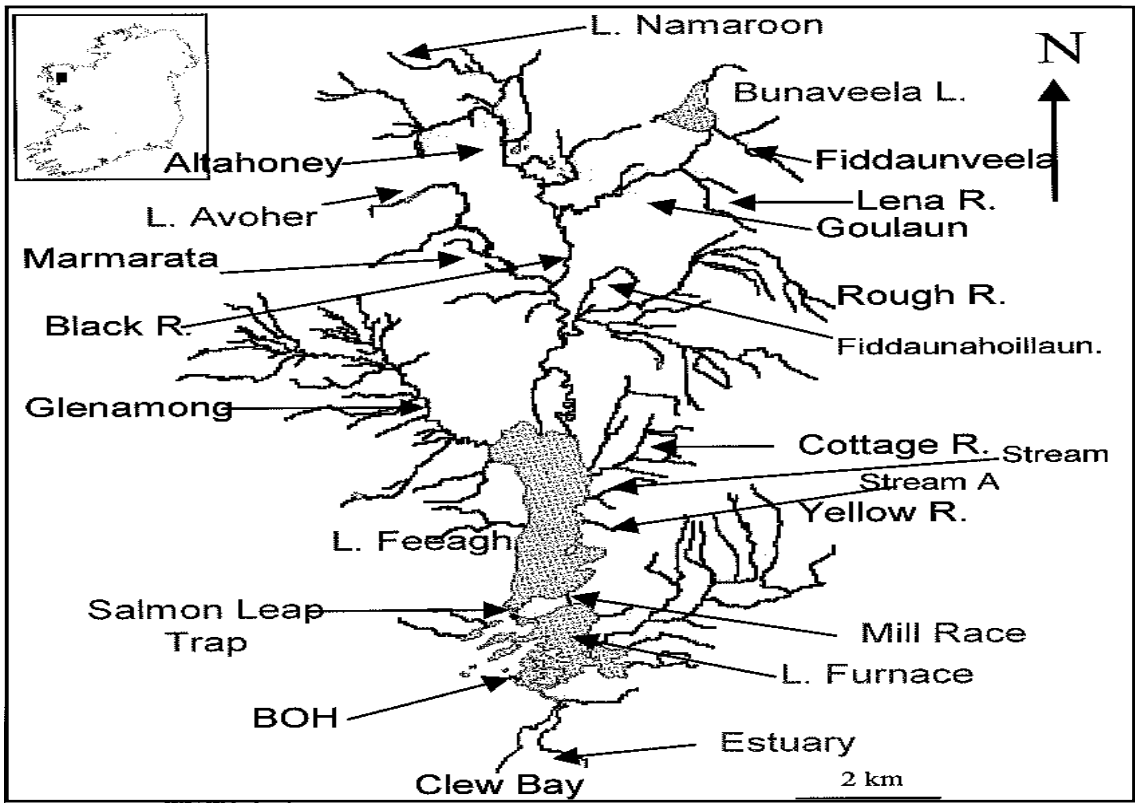


Figure 4.1 Map of Burrishoole Catchment Newport Co. Mayo showing the main lakes and rivers (Poole *et al.*)[152]

The lake is surrounded by high mountainous terrain on three sides to the North, West and East of the lake and fed by the Glenamong and Strathmore (Black River) rivers in the north and drains into Lough Furnace in the south and from there into Clew Bay and finally the Atlantic. It is a pristine environment reportedly untouched by industry and with little agriculture.[152] Recent studies carried out by the Marine Institute (MI) in the

Burrishoole region have reported elevated levels of higher chlorinated dibenzo-dioxins (PCDD) in the biota of the native eels (*Anguilla anguilla*) present in these waters.[153] Mc Hugh *et al.* [153] report that the European eel is a high lipid, long lived species which can accumulate contaminants from their environment making them ideal bio-monitor organisms. The study reports that high levels of PCDDs were found in the lipid of the animals sampled in the Burrishoole catchment in comparison to animals sampled from outside the region. Of the eels from the Burrishoole catchment the PCDD/F fraction of contaminants analysed was dominated by the octachlorinated dibenzo-p-dioxin (OCDD) congener. This was confirmed by Covaci *et al.* [154] who also identified this congener in samples of the eels from this region along with number of chromatographic peaks characteristic for Chlorinated Diphenyl Ethers (PCDEs, specifically diHO-Octa-CDE and di-HO monoBr-Hepta-CDE) and methoxy substituted PCDEs as having a signal much more intense than that of PBDEs. Covaci *et al.* [154] further report that while PCP levels may be historic in origin, it is not uncommon for the parent PCP to be at low concentrations in biota, with the more persistent by-products of the manufacture of PCP (*e.g.* OCDD and PCDEs) being accumulated within biota.

Geyer [27] reports that OCDD is a "super-hydrophobic" compound with a high bioaccumulation factor which is often associated with pentachlorophenol production and use. This study, among others, suggests that compounds such as pentachlorophenol (PCP) can act as a potential point source input to the Burrishoole eel population and that the profile of PCDD in the eels and other matrices resembles that of technical PCP. [155,156,27,157,158,159] It is important to note however that to this author's knowledge there is no information relating to the use of PCP at any stage in the Burrishoole region however there are reports of its use in Ireland.[160]

To investigate this hypothesis this chapter documents the use of passive samplers in conjunction with biota and sediment to investigate the Burrishoole region and attempt to gain any insights into possible sources of contamination present and if possible to identify possible influences. The sampling and analysis discussed below further supplement the original findings of Mc Hugh *et al.*[153]

4.1.1 Sampling in Burrishoole – Design and Perspectives

To investigate the region for potential point sources of dioxin contamination in resident eels present, and the levels of contaminants (PAH and PCB/OC) in the region as a whole, it was firstly important to formulate a sampling plan that would incorporate the elements necessary to give a complete picture of the levels of contaminants present in the local environment. It was therefore important to ask various pertinent questions and to tailor the sampling plan in a manner which could supply answers to them. Hence some of the questions arising from the previous MI study [153] are discussed below:

1. Are the elevated dioxin levels found in the previous study still present in the local eel population? Is it species dependent?
2. If present how would the levels vary between smaller younger animals and the larger older animals?
3. Can PCP or PCDD/F be found in the sediment and at what levels? Can it be found in the water column? What about the levels of other POPs?
4. Can passive sampling devices be used to estimate the levels of contaminants in the water column? Can it be used to detect PCP or PCDD/F?
5. Could principal component analysis be used to pinpoint a potential source of any PCDD/F.

With these questions in mind a sampling plan was implemented which would incorporate many aspects of environmental analysis. It was thought important to sample the local water, animals and sediment for a variety of contaminants in the hope that a potential PCDD source could be identified. In the environment sediment, as the final sink of many organic hydrophobic contaminants, provides a good "snap-shot" of the general status of an area regarding the presence of POPs. These contaminants in isolated areas are generally transported via air until they enter the water mass and are sorbed onto suspended particulate matter where they sink to form a water bottom sediment layer. From here benthic organisms can accumulate these lipophilic contaminants and they can then enter the food chain where they can be accumulated to many times higher than the background levels by apex predators. The eel may be considered a predator at the top of its food web. Water borne dissolved concentrations of these contaminants could also provide useful information so it was decided to use PSDs as they can accumulate POPs to a higher concentration allowing easier determination analytically. An overview of the individual elements of the study is given below:

1. Collection and analysis of biota – local eels (*Anguilla anguilla*) along with any local fish which could be sampled. These would be analysed for dioxins and other contaminants;
2. Sediment – collected from various locations within the catchment for the analysis of contaminants including PCP among others (PCB/OC and PAHs);
3. Water sampling – passive samplers would be deployed to determine levels of all bio-available hydrophobic contaminants present in the region.

4.1.2 Location of Sampling Carried out in the Burrishoole Region

After discussions with MI staff stationed at Newport it was decided to sample the local eel and trout population in Lough Feeagh and Furnace as well as Lough Bunevella. Sediment samples were collected in these areas as well as Gallaghers Lake located close to Lough Feeagh. Passive samplers were deployed at all of the above sites and outside the catchment (site E to H) as shown in *Fig. 4.2* below. Further to this, the exact locations within the catchment are shown below (*Table 4.1*) in a latitude and longitude format to allow the exact location be known apart from sites outside the catchment.

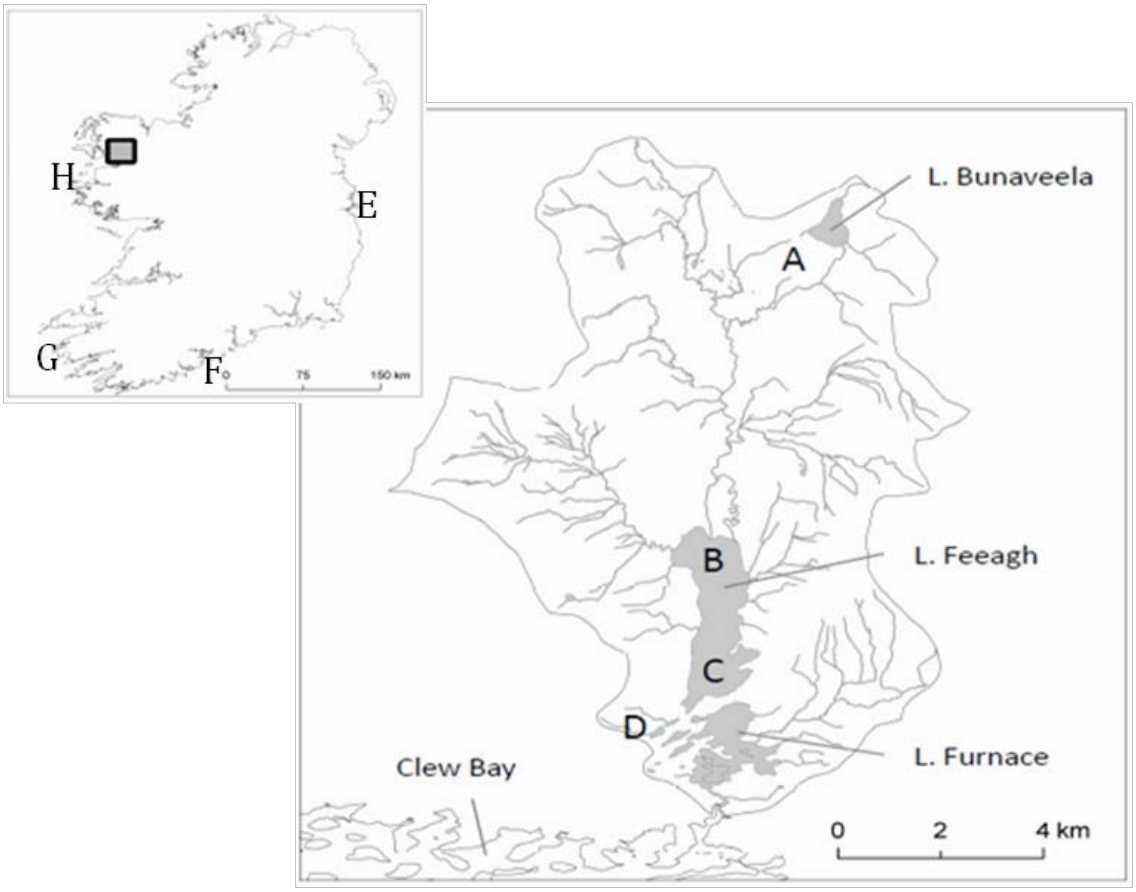


Figure 4.2 Sampling locations in the Burrishoole catchment carried out during the summer/autumn 2009.

Table 4.1 Longitude and latitude coordinates of sampling locations in the Burrishoole catchment during the summer/autumn 2009.

Location	Coordinates
Black river	53N 57' 20.04N, -9 34' 50.59W
Eel weir	53N 55' 30.87N, -9 34' 43.49W
Lough Bunevella	54N 02' 14.86N, -9 32' 57.94W
Gallaghers Lake	53N 55' 40.78N, -9 32' 18.11W

***Site A**: Lough Bunevella, Burrishoole Co.Mayo.*

Lough Bunevella lies approximately 150 m above sea level at the head of the Goulaun sub-catchment. It has a maximum depth of 23 m and has one inflowing (the Fiddaunvella) and one out-flowing stream (the Goulaun) and feeds into Lough Feeagh. The site itself is accessible to salmon, trout and char as well as eels. Bunevella L. is surrounded by high mountainous terrain on all sides and is in a remote location.[152] There is little in the way of agriculture or boat use in the Lough. The site is at the top of the catchment system and it was decided that deployment in this location would give an indication if any potential contamination source was present in this area.

***Site B:** Black River, Lough Feeagh, Burrishoole.*

Lough Feeagh is an oligotrophic lake of glacial origin with a maximum depth of 45 m and an average temperature range of 3 – 20^{o}C. The pH of the lake is generally 6.3 -7.0 and conductivity values are around 80-90 µs/cm. The waters of Lough Feeagh are coloured and only moderately transparent,[152] it is also surrounded on three sides by mountainous terrain, draining into Lough Furnace from the southern corner of the lake. Again there is little industry located in the region however some forestry has taken place to the west in the drainage area of the Glenamong River. The Black River, along with the Glenamong drains directly into Lough Feeagh at this site. The site is therefore an

important indicator of the location of any potential contaminant input from the west, along the Glenamong River or from L Bunevella in the north via the Black River.

Site C *eel weir, Lough Feeagh, Co.Mayo*

This location was in the south of Lough Feeagh and as such was an important indicator of any contamination issues in the lake itself as opposed to further up the system in Lough Bunevella. The site itself is close to a pier that is occasionally used to launch small boats.

Site D *Gallaghers Lake, Lough Feeagh, Co.Mayo*

Gallaghers Lake is located to the west of Lough Feeagh and is the smallest lake present with a max depth of 4 m. The water present is a distinct brown peat colour and as a result transparency is moderate. The Lake appears to be isolated from the Lough Feeagh system in that no direct mixing of these waters takes place on the surface.

The sites outside the catchment which had passive samplers deployed included the Omey Island control site, Dublin, Cork and Bantry bay. The data generated from deployments in these locations were used to compare with samplers deployed in the catchment.

4.2 Sampling and analysis of Biological tissue

Since the European eel (*Anguilla anguilla*) is a long lived, high lipid species which is capable of living in a variety of environments it is therefore a suitable 'bio-indicator' species which has been used in many studies for the determination of organic contaminants.[153] It was therefore sampled as the primary species in this study, however

other species that were caught during the sampling period (trout) were also used. Samples were collected in this study using eel-pots and fyke nets. Once procured the samples were placed in a freezer (-20^{o}C) for storage before being removed to the MI laboratory for final storage. Samples were allowed to thaw to room temperature before being measured, separated by size (<40 cm – 60 cm<) and a section of subcutaneous lipid was removed using a scalpel. The lipid was then pooled and homogenised before being weighted out to a clean beaker and placed back in storage in a freezer (-28^{o}C). Eel and trout measurement data collected is shown below (*Table* 4.2).

Table 4.2 Sampling details, including length (mm) and extractable lipid (%) from pooled eel and trout samples collected in the Burrishoole catchment.

Ecotype	**Silver eel**	**Yellow eel**	**Brown Trout**
Location	**L.Furnace**	**L.Feeagh**	**Lough Bunevella**
MI Reference	**MSC/09/1275**	**MSC/09/1274**	**MSC/09/1273/1**
Individuals (n)	14	5	15
Length Mean (cm)	16.4	26.0	43.6
Standard deviation (cm)	2.1	3.0	9.5
Extractable lipid %	5.5	15.6	0.3

Yellow eels are sexually immature animals and hence younger animals which spend 5 – 20 years in fresh water before becoming sexually mature silver eels. It is known that not all yellow eels will manage to go to sea to reproduce and as such some yellow eels will inhabit and feed/grow in estuaries and lakes for their lifetime but never become silver eels. Yellow eels can build up lipid reserves in preparation to spawn but this may never take place, conversely current research also suggests that the lipid content in silver eels may not be high enough to sustain the migration process, thus lipid values in the sampled eels may be reflective of the current thinking in terms of eel migration.[161] The samples were then sent to Eurofins GfA Gmbh in Germany where they were allowed to defrost before they were further homogenised using an ultra turrax and extracted using solid/liquid extraction. The extract was cleaned up using a carbon on glass fibre

multicolumn before analysis occurred on a Finnigan MAT 95 XL high resolution GCMSMS with a DB-5 60 m column. Eurofins are reluctant to give details of their total extraction and analysis methods beyond what was described in this section.

4.2.1 Burrishoole Biota - Dioxin Results and Discussion

Biota samples were sent to Eurofins GfA Gmbh in Germany under subcontract and were analysed in the manner described in the previous section with the following results for dioxins/furans shown (*Table 4.3*) below.

Table 4.3 Upper-bound results for dioxins/furans (pg/g w w) from Biota samples collected from the Burrishoole catchment in the summer/autumn 2009.

Matrix	**Eel (Silver)**	**Eel (Yellow)**	**Trout**
Lipid extractable	**5.48**	**15.6**	**0.32**
Compound	**MSC/09/1275 pg/g**	**MSC/09/1274 pg/g**	**MSC/09/1273/1 pg/g**
2,3,7,8-TetraCDD	0.01	0.04	0.01
1,2,3,7,8-PentaCDD	0.07	0.67	0.07
1,2,3,4,7,8-HexaCDD	0.05	0.75	0.06
1,2,3,6,7,8-HexaCDD	0.14	2.14	0.16
1,2,3,7,8,9-HexaCDD	0.05	0.70	0.05
1,2,3,4,6,7,8-HeptaCDD	0.26	3.96	0.30
OctaCDD	2.07	16.9	2.42
Furans			
2,3,7,8-TetraCDF	0.03	0.03	0.03
1,2,3,7,8-PentaCDF	0.01	0.03	0.02
2,3,4,7,8-PentaCDF	0.03	0.12	0.04
1,2,3,4,7,8-HexaCDF	0.01	0.08	0.02
1,2,3,6,7,8-HexaCDF	0.01	0.06	0.02
1,2,3,7,8,9-HexaCDF	0.02	0.03	0.02
2,3,4,6,7,8-HexaCDF	0.02	0.07	0.02
1,2,3,4,6,7,8-HeptaCDF	0.02	0.09	0.03
1,2,3,4,7,8,9-HeptaCDF	0.02	0.04	0.03
OctaCDF	0.12	0.22	0.14
∑PCDD	2.65	25.2	3.07
∑PCDF	0.29	0.77	0.37
∑PCDD/F	2.94	25.9	3.44

The upper bound ∑PCDD/F (pg/g w w) ranged from 2.94 - 25.9 pg/g which compared well to the study by Mc Hugh *et al.* [153] where ∑PCDD/F (pg/g w w) in the animals from the Burrishoole region ranged from 22.5 – 78.6 pg/g w w. Mc Hugh *et al.* [153] also report on concentrations of ∑PCDD/F from animals outside the Burrishoole region which were found to range from 1.04 – 1.29 pg/g w w. The upper bound ∑PCDD (pg/g w w) ranged from 2.65 – 25.2 pg/g which also compares well with the work of Mc Hugh *et al.* [153] where ∑PCDD (pg/g^{-1} w w) ranged from 22.2 – 77.6 pg/g for animals inside the Burrishoole catchment and 0.62 – 0.81 pg/g for those animals from outside the catchment. The upper bound ∑PCDF (pg/g w w) values range from 0.29 – 0.77 pg/g which again compares well with the study by Mc Hugh *et al.* [153] where ∑PCDF (pg/g w w) ranged from 0.26 – 1.01 pg/g for animals inside the Burrishoole catchment and 0.42 – 0.52 pg/g for those animals from outside the catchment. This would indicate that the PCDD/F profile present in the Burrishoole catchment reported by Mc Hugh *et al.* [153] is still present in the region and further that it is not a species specific phenomenon as the use of native trout samples also showed this profile.

A report by Geeraerts *et al.* [162] on levels of PCDD/F in Belgian eels indicate a mean ∑PCDD/F (pg/g w w) value of 8.0 pg/g w w with a maximum value of 110.5 pg/g w w. These results are on a similar scale to the results presented in this study. To compare these PCDD/F levels and profiles with those of other studies the results had toxic equivalency (TEQ) values applied to them. Complementary results for this study are shown in appendix A.7 *Table 1*. Upper bound ∑PCDD/F WHO-TEQ (pg/g w w) eel values ranged from 1.95 – 7.9 pg/g w w in comparison to 0.21 – 4.37 pg/g w w reported by Mc Hugh *et al.* [153] A report by Szlinder-Richert *et al.* [163] on eels from Poland reported upper bound ∑PCDD/F WHO-TEQ (pg/g^{-1} w w) concentrations ranging from 0.31 – 1.88 pg/g w w which are on a similar scale to those presented in this study.

PCDDs contribute the majority of the body burden present for ∑PCDD/F in 2009 Burrishoole eels ranging from 90.4 to 97.0% of the total PCDD/F contaminant burden. This compares favourably with the results reported by Mc Hugh *et al.* [153] where the PCDD in 2005 to 2007 eels from the Burrishoole comprised approximately 98% PCDDs compared to an average of 64.0% PCDDs in the eels measured from other areas in Ireland. The OCDD PCDD congener contributes the majority of the body burden to these animals with values ranging from 65.2 – 70.6 % of total upper bound ∑PCDD/F (pg/g w w) found. This compares to 53.4 – 58.7 % contribution of OCDD to the ∑PCDD/F (pg/g w w) reported by Mc Hugh *et al.* [153] in eels from the Burrishoole and 23.3 – 28.8 % from those animals from outside the catchment. The percentage congener contribution to the ∑PCDD/F (pg/g w w), when placed in a graph as below (*Fig* 4.3) closely resembles that of the percentage congener contribution found in technical PCP.[164]

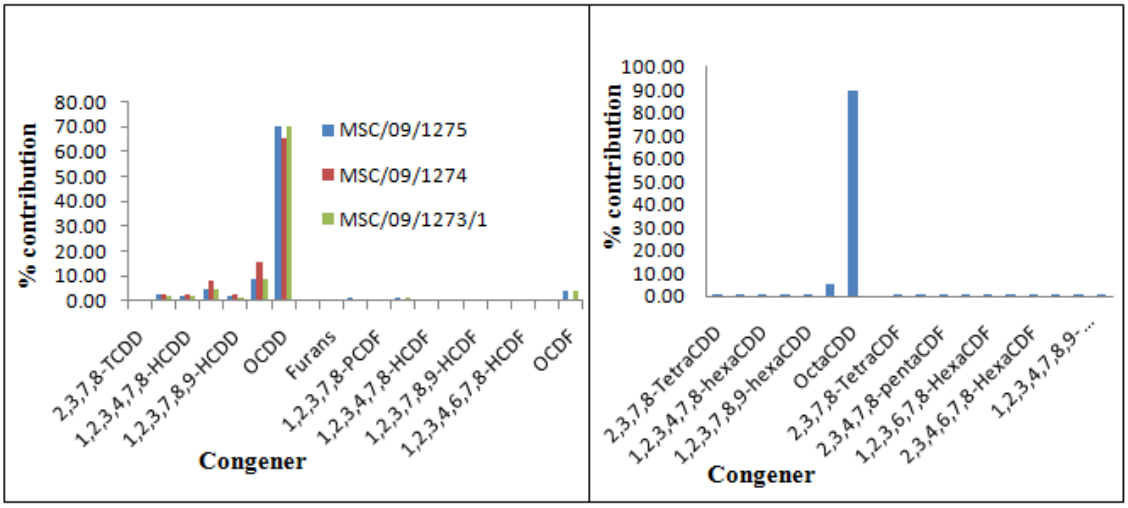


Figure 4.3 Comparison of the percentage PCDD congener contribution from eels and trout at the Burrishoole (A) to that of technical PCP (B) (reproduced from Birch *et al.*) [164]

Total furan concentrations for both 2009 eel samples (0.23 and 0.74 pg/g w w), is in agreement with observations of McHugh *et al.* [153] who reported 0.25 to 0.99 and 0.36 to 0.49 pg/g (w w) in Burrishoole and Irish eels respectively. PCDF levels in Burrishoole Eels are in overall agreement with those from other locations in Ireland therefore it can

be concluded that the increased PCDD component in Burrishoole eels is likely to derive from a discrete point source PCDD influence.

4.2.2 Burrishoole Biota PCB Results

Results presented (*Table 4.4*) below show the PCB concentration data (pg/g w w and ng/g w w) for eel and trout samples from the Burrishoole catchment.

Table 4.4 Concentrations of dioxin like PCBs (pg/g w w) and marker PCBs (ng/g w w) along with WHO-TEQ values (pg/g w w) for PCBs in eels and trout samples from the Burrishoole catchment.

Matrix	**Eel (Silver)**	**Eel (Yellow)**	**Trout**
Lipid%	5.48	15.6	0.32
Compound	MSC/09/1275 pg/g	MSC/09/1274 pg/g	MSC/09/1273/1 pg/g
DL-PCBs			
Mono ortho			
PCB 77	0.54	1.01	0.63
PCB 81	0.11	0.20	0.13
PCB 126	0.47	1.84	0.54
PCB 169	0.54	1.39	0.63
Non-ortho			
PCB 105	61.1	94.4	72.8
PCB 114	3.09	3.57	3.45
PCB 118	244	375	291
PCB 123	2.82	4.76	4.26
PCB 156	33.7	42.6	40.2
PCB 157	7.15	12.3	8.51
PCB 167	16.3	46.1	20.5
PCB 189	2.59	13.0	3.19
∑DL-PCBs	372	596	446
∑DL-PCB WHO TEQs	0.11	0.28	0.12
$\sum PCB_7$			
PCB 28	15.7	43.8	18.4
PCB 52	42.7	155	48.8
PCB 118	244	375	291
PCB 101	69.4	224	81.7
PCB 138	370	940	440
PCB 153	657	1,940	755
PCB 180	179	659	220
$\sum PCB_7$	1,578	4,337	1,855

PCB compounds in the Burrishoole biota samples were low overall which is to be expected from such a remote area with little in the way of industrialisation. The ∑DL-

PCBs pg/g w w calculated ranged from 372 – 596 pg/g w w which are lower than those reported by Mc Hugh *et al.* [153] where the values ranged from 372 – 4364 pg/g w w. The levels of ∑DL-PCBs pg/g in Burrishoole eel samples is low in comparison to those reported by Geeraerts *et al.* [162] where levels ranged from 2419 – 409152 pg/g w w in eels from Belgium. The ∑DL-PCBs WHO TEQ accounted for 18.7– 46.4% of the total ∑PCDD/F-DL-PCBs WHO TEQ (pg/g w w) body burden present in these animals. This is in contrast to Geeaerts *et al.* [162] who suggest that DL-PCBs account for (mean) 91% of the total TEQ values regardless of sampling site. A report by Szlinder-Richert *et al.* [163] suggests that DL-PCBs contribute an average of 57.8 % to the total WHO TEQ (pg/g w w) while Stachel *et al.* [165] report that DL-PCBs contribute an average of 78.3% to the total WHO-TEQ (pg/g w w) burden to German eel which is very different to the profile found in the Burrishoole. Knutzen *et al.* [166] report that ∑DL-PCBs range from 16.9 – 21.3 % of the total WHO TEQ (pg/g w w) burden to eels found in Norway near a dioxin 'incident' at the Grenland fjord site.

$\sum PCB_7$ ng/g w w ranged from 1.58 – 4.34 ng/g which compares well to the eel concentrations of marker PCBs reported by Mc Hugh *et al.* [153] and is also low in comparison to values ranging up to 1512 ng g^{-1} reported by Santillo *et al.* [167] PCB 153 was the dominant congener overall for the marker PCBs with an average percentage contribution of 42.4 %. There was also a major contribution from PCB 138 (22.9%). This compared well with McHugh *et al.* [153] where PCB 153 contributed an average of 32.4 % of the marker PCB burden.

4.2.3 Conclusion - Burrishoole Biota Results

In section 4.1.1 various questions were asked regarding the elevated PCDD/F concentrations reported by McHugh *et al.* [153] in the indigenous Burrishoole eels. The eels sampled in this study suggest that the elevated PCDD/F levels are still present in the Burrishoole and that they are not a species specific phenomenon as PCDD/F levels in trout also show this profile. Lipid normalised concentrations of PCDD/Fs (pg/g w w) in the eels in particular and the domination of the total burden of ∑PCDD/Fs by the OCDD congener also supports the data presented by the Mc Hugh *et al.* [153] study. Levels of PCDD/F in the Burrishoole eels are elevated compared to the study on eels from across Belgium by Geeraerts *et al.* [162] (apart from one site) while the ∑PCDD/F WHO-TEQ values (pg/g) were higher than that of eels from Poland reported by Szliner-Richert.[163] The ratio of ∑PCDD/F WHO-TEQs (pg/g) to that of ∑DL-PCBs WHO-TEQs (pg/g) is higher than that reported by Stachel *et al.* [165] for German eels and for Geeraerts *et al.* [162] and more closely resembles that reported by Knutzen *et al.* [166] in eels sampled near a known dioxin incident. PCB concentrations reported by Mc Hugh *et al.* [153] are similar to those reported here while these results are lower than those reported by Geeraerts *et al.* [162] and by Szlinder-Richert *et al.* [163] This would indicate that while the levels of PCBs are low compared to studies from Europe the ratio of DL-PCBs to PCDD/Fs indicates that the PCDD/Fs are elevated in the Burrishoole catchment.

4.3 Sampling and Analysis of Sediment from Burrishoole

Sediment is regarded as the final sink for many compounds including pesticides and herbicides and as such is regarded as an important matrix for the determination of the presence of contaminants and so will be used in this study.[10] Sediment was collected using a Van Veem sediment grab and placed in a clean solvent washed glass jar before

being transported back to the laboratory. Samples were homogenised and the 63 µm fraction was sieved and retained before being freeze dried and placed in solvent washed glass jars. They were placed in the freezer (-28^{o}C) until they were analysed using GC-ECD and GC-MS using the optimised conditions as described in chapter 3.

4.3.1 Extraction and analysis of sediment

Sediment samples collected at the Burrishoole catchment were extracted following the procedure outlined in section 3.4.1.1. Results for the extraction and analysis of sediment from the Burrishoole region are broken down into results for PAHs, PCB/OC, PCP/PCA and PCDD/F analysis which are shown in (*Table 4.5*) below. PCB/OC and PCDD/F data are generated from a composite sediment sample.

4.3.1.1 Results for PAH in Burrishoole Sediment

Sediment from the selected Burrishoole sites was analysed using the GC-MS optimised programme described in chapter 3. The results, measured in ng/g dry weight (d w) are shown (*Table 4.5*) below. Naphthalene values were removed from the results due to elevated levels found in the blank. The results for PAHs found in Burrishoole range from 0.2 ng/g for benzo(g,h,i)perylene found in the eel Weir sediment to 171.4 ng/g of benzo(b)fluoranthene found in Lough Bunevella.. The Lough Bunevella sample showed the highest levels of PAHs present at 789.9 ng/g d w with the lowest concentrations to be found in the eel Weir 36.9 ng/g d w.

These values are low in comparison with those reported by Cachot *et al.* [23] from the Seine in Paris which show $\sum PAH_{21}$ 12492 ng/g d w and 12210 ng/g d w for $\sum PAH_{17}$. Hale *et al.* [168] showed that the levels of $\sum PAH_{16}$ USEPA at various sites in the river

Tyne in the northeast of England were 16400 ± 7300 µg/g. Charlseworth *et al.* [169] reported that the $\sum PAH_{15}$ from the Western Irish sea were below 100 ng/g d w for sandy sediments and below 1422 ng/g d w in a mud basin with many of the sites sampled being above 1000 ng/g d w. These results would be consistent with results found in the Burrishoole catchment with the sandy sediment at the eel Weir being below 100 ng/g (36.9 ng/g d w) and typical of concentrations for the muddier samples at the other locations. The comparison of levels from the Black River and eel Weir shows a large variation in concentration. This may be primarily due to the sediment types found in these regions. The Black River sediment was dark and peaty whereas the eel Weir sediment was sandy in nature. Lough Bunevella had the highest concentration levels present in the catchment (∑PAH 789.9 ng/g d w) and in particular elevated concentration levels of benzo(a)anthracene, benzo(b)fluoranthene and benzo(a)pyrene were found.

These compounds as well as fluoranthene, pyrene and indeno(1,2,3-c,d)pyrene, which are also elevated show that the petroleum derived low molecular weight PAHs are not present in large quantities indicating that the sources for PAH in the area are primarily of pyrolytic (fossil fuel combustion and vegetation fires) origin. The composition and distribution of individual PAH congeners found throughout the catchment region is illustrated (*Fig. 4.4)* below.

PAH profiling can allow an identification and characterisation be made of the sources of PAH contamination present in this system by analysing the ratio of various PAHs as described in section 1.3.3. To assess the main sources of PAHs present in the Burrishoole catchment the ratio of fluoranthene to pyrene was used. The ratio of the sum of low molecular weight PAHs ∑LPAHs) (2-3 ring compounds) to the sum of

higher molecular weight PAHs ∑HPAHs) (4–6 rings) is < 1 suggesting that PAHs in the Burishoole sediments are mainly of pyrolytic origin apart from the eel Weir which may have a mixed origin. Sediment from this section of Lough Feeagh was sandy in nature which may have affected this measurement as there is less of the <63 µm fraction available for analysis in sediments of this type. The site itself was close to a jetty which was used to launch boats perhaps providing localised petrogenic PAHs at this site.

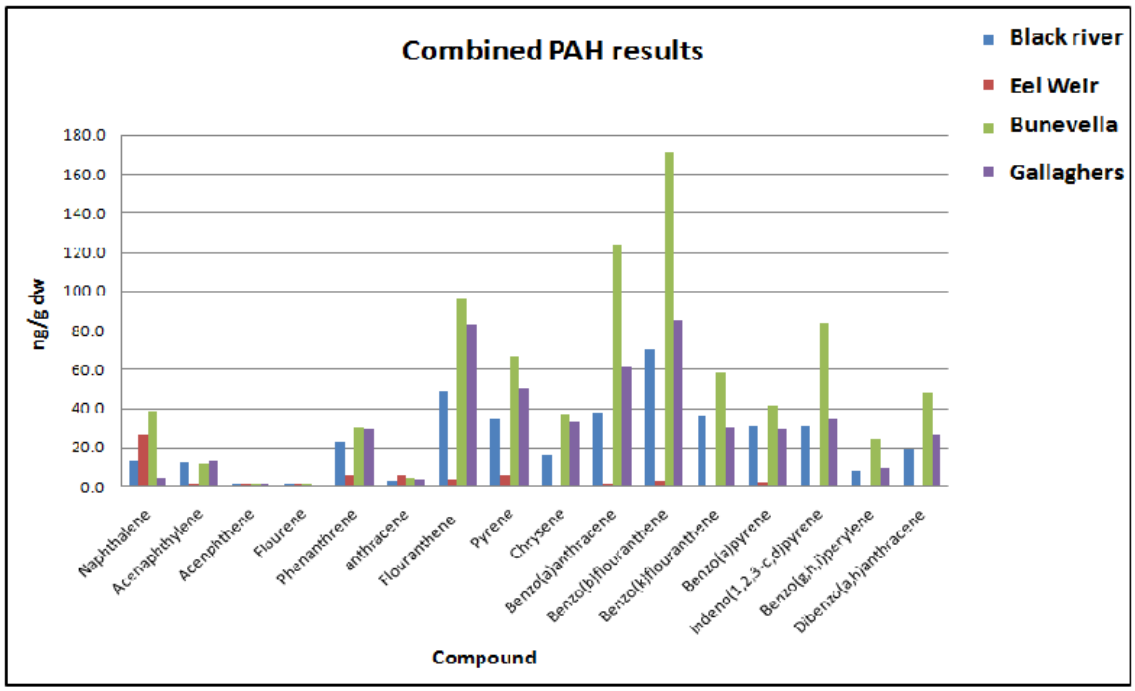


Figure 4.4 Concentration (ng/g d w) and distribution of PAHs found in the Burrishoole catchment analysed using the GC-MS under optimised conditions.

Table 4.5 Upperbound concentrations (ng/g d w) for the analysis of sediment for PAH/PCB/OC, PCP/PClA and PCDD/F (pg/g d w) from the Burrishoole catchment.

Compound (ng/g dw)	Black River	Eel weir	Bunevella	Gallaghers
PAH				
Acenaphthylene	12.5	1.97	11.4	12.9
Acenphthene	1.98	1.65	1.99	1.95
Fluorene	1.50	1.45	1.90	1.23
Phenanthrene	22.7	5.52	30.2	29.2
anthracene	3.26	5.36	4.00	3.45
Fluoranthene	48.4	3.79	95.9	82.8
Pyrene	35.1	5.39	66.3	50.3
Chrysene	16.3	1.00	36.7	33.5
Benzo(a)anthracene	37.5	1.87	124	61.9
Benzo(b)fluoranthene	70.2	3.13	171	85.2
Benzo(k)fluoranthene	35.8	0.89	58.8	30.4
Benzo(a)pyrene	31.6	2.27	41.1	29.7
Indeno(1,2,3-c,d)pyrene	31.5	1.10	83.4	34.8
Benzo(g,h,i)perylene	8.28	0.23	24.1	9.7
Dibenzo(a,h)anthracene	19.7	1.23	47.8	26.6
∑PAHs	376	36.9	799	494
∑LPAHs	42.0	16.0	49.5	48.7
∑HPAHs	334	20.9	749	445
Ratio	0.13	0.76	0.07	0.11
PCB/OC (ng/g dw) (Composite sample)				
HCB	0.08	PCB 105	0.01	
PCB 28	0.03	PCB 118	0.11	
PCB 31	0.02	PCB 138	0.12	
PCB 44	0.05	PCB 153	0.15	
PCB 52	0.06	PCB 156	0.02	
PCB 101	0.08	PCB 180	0.09	
pp-DDE	0.23	PCB 194	0.01	
		PCB 209	0.001	
PCP/PClA (ng/g dw)		1.60	0.64	1.28
Control	0.51			
PCDD/F (pg/g dw) (Composite sample)				
2,3,7,8-TetraCDD	0.001		1,2,3,7,8-pentaCDF	0.001
1,2,3,7,8-pentaCDD	0.002		2,3,4,7,8-pentaCDF	0.01
1,2,3,4,7,8-hexaCDD	0.01		1,2,3,4,7,8-HexaCDF	0.01
1,2,3,6,7,8-hexaCDD	0.01		1,2,3,6,7,8-HexaCDF	0.01
1,2,3,7,8,9-hexaCDD	0.01		1,2,3,7,8,9-HexaCDF	0.0001
1,2,3,4,6,7,8-heptaCDD	0.15		2,3,4,6,7,8-HexaCDF	0.004
OctaCDD	2.34		1,2,3,4,6,7,8-HeptaCDF	0.03
			1,2,3,4,7,8,9-HeptaCDF	0.003
2,3,7,8-TetraCDF	0.01		OctaCDF	0.03

4.3.1.2 Results for PCB/OC and PCP/PClA in Burrishoole Sediment

Composite sediment samples collected from the Burrishoole catchment were prepared and analysed for PCB and OC contaminants using the GC-ECD under optimised conditions as specified in chapter 3. The results for PCB/OCs in sediment from Burrishoole are shown (*Table 4.5*) above. The results for PCB and OCs found in the Burrishoole are low overall which is to be expected from this remote area with little in the way of industrialisation. HCB levels are low (0.08 ng/g d w) in sediment from the region in comparison to a global average of 0.68 ng/g d w and contaminated areas of northern European and Russian levels of 5.20 and 4.83 ng/g d w respectively reported by Barber *et al*.[170] Sediment from the Burrishoole region (-63 µm fraction) along with a reference sample (Kinvara, Co. Galway) was further analysed by the Institute for Environmental Studies (IVM) in the Netherlands for analysis of PCP and PClA. The results show elevated levels of PCP/PClA in comparison to the reference site with the highest levels found at the eel Weir (1.60 ng/g d w) and Gallaghers Lake (1.28 ng/g d w) with the lowest levels found in L. Bunevella (0.64 ng/g d w) while the reference site (Kinvara) also exhibited levels of PCP/PClA (0.51 ng/g d w).

4.3.1.3 Results for PCDD/F in Burrishoole Sediment

A remaining composite sediment sample from the Burrishoole region consisting of the remainder of sediment from all three sites was sent to Eurofins Gmbh where it was analysed for PCDD/Fs the results of which are shown in *Table 4.5*. The ∑PCDD/F concentrations (ng/g d w) are dominated by the PCDD fraction which makes up 96.4 % of the total levels found in the sediment sample. There are major contributions from the hexa- and heptaCDD congeners however OCDD dominates the ∑PCDD/F accounting for 90 % overall. This compares well to the results reported by Sanctorum *et al.* [171] in

sediment samples from the Yser and upper Scheldt rivers where the OCDD congener accounts for 73 – 85 % of the overall ∑PCDD/F concentration found. The PCDD/F percentage congener profile reported in the Sanctorum study [171] cited a possible PCP source and also closely resembles the profile shown (*Figure 4.5*) below. This profile also closely resembles that reported by Birch *et al.* [164] for sediments from areas of Homebush Bay and Port Jackson, Australia where OCDD and higher chlorinated dioxin congeners are dominant and a potential input source at these site was identified as being related to chemicals produced (including PCP) on the Rhodes Peninsula. Masunaga *et al.* [172] report that using PCDD/F congener specific information it was possible to identify point source impacts in the Tokyo Bay basin. A further three sources were identified which included PCP and chloronitrophen (CNP) production, and combustion sources. The sediment samples identified as having a PCP source were all dominated by the OCDD dioxin congener.

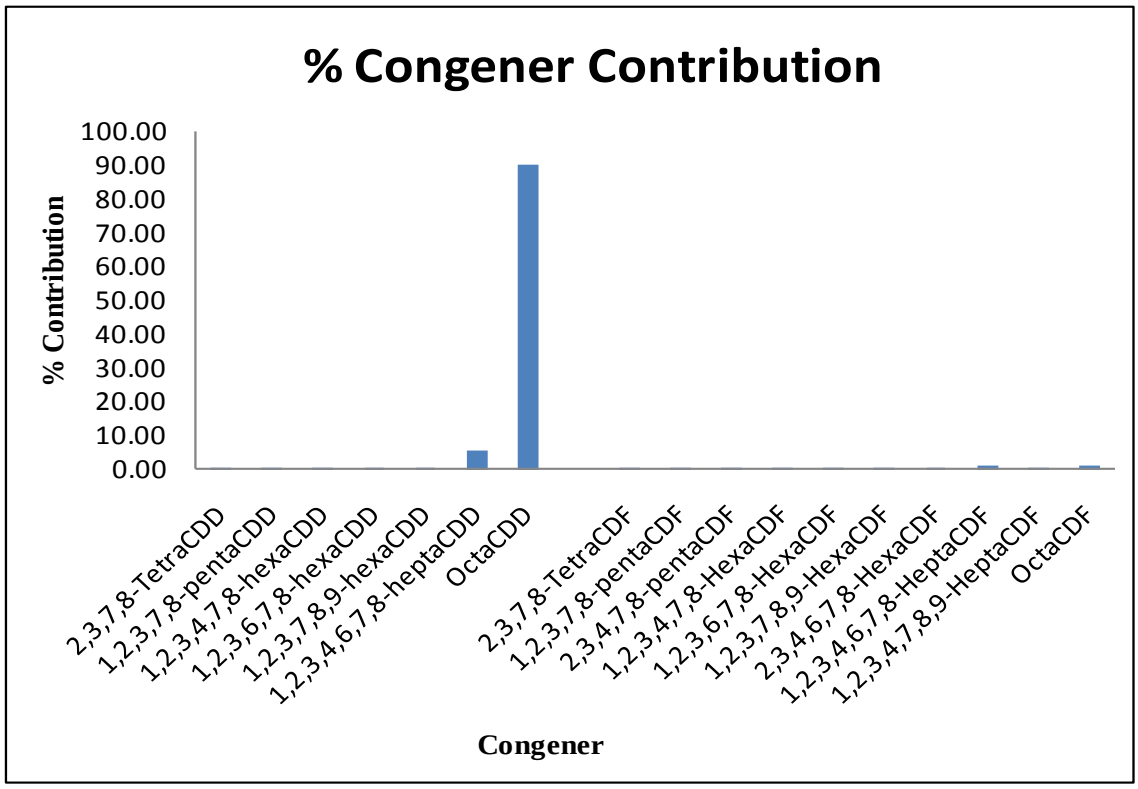


Figure 4.5 PCDD/F percentage congener contributions from a composite sediment sample from the Burrishoole catchment.

4.3.1.4 Conclusion for Burrishoole Sediment.

The Burrishoole sediment showed low levels of contaminants overall which is to be expected in an isolated area with little or no industrialisation. The origin of PAHs in the region (pyrolytic) supports this hypothesis. PCB/OC levels present in the sample were also low. PCP/PClA analysis showed that while levels in Burrishoole sediments were not elevated relative to the reference site, they do exceed those from the reference location. The PCDD/F concentration in the composite Burrishoole sediment sample showed OCDD being the dominant congener comprising 90 % of the ∑PCDD/F burden which is in good agreement with that found in the biota samples.

4.4 The Use of Passive Samplers in the Burrishoole Region

PDMS passive sampling devices were deployed in the Burrishoole region using the method detailed in appendix A.6 for an extended period beginning in June 2009 with the deployment of a single passive sampler in Lough Bunevella (54 1' 16.26N -9 32' 58.89W), which was used to test the structural integrity of the passive sampling set up. This represented the first such deployment during this project. The PSD at Lough Bunevella was left for an extended sampling period of 110 days before being retrieved allowing further deployments of PSD devices in other locations around the catchment as shown in *Fig 4.2*. This second deployment (3 months) of 4 PSDs was collected in December 2009, before being returned to the laboratory and stored, along with the first PSD, at -28^{o}C in the MI laboratories. All PSDs were retrieved intact with no loss of PDMS sampler sheets or cages. The fact that the samplers were deployed and retrieved with no losses shows that the passive sampler setup for PDMS PSDs is adequate for sampling in inland lakes.

The initial passive sampler from Lough Bunevella was analysed first to allow for familiarisation with the extraction and analysis techniques to ensure successful analysis of subsequent samples. The preparation, deployment, retrieval, extraction and analysis of the samplers deployed in the Burrishoole are discussed in appendix A.6. with the calculation of results discussed in the following sections.

4.4.1 Calculation of Dissolved Water Concentration for Lough Bunevella PSDs.

The calculation of C_w concentrations found by the PSDs in Lough Bunevella was calculated in a stepwise manner:

1. Calculation of responses for PRCs found in field control, preparation controls and in exposed samplers, and the calculation of *in-situ* sampling rates (R_s),
2. Addition of internal standards and calculation of concentrations (ng/g) in the PSDs, including quality control information,
3. Calculation of C_w concentrations from PSDs.

Once the method for calculating the C_w for Lough Bunevella was completed it was then used to complete estimations for dissolved water concentrations in all exposed samplers in the region.

4.4.2 Calculation of *In Situ* Sampling Rates (R_s)

The calculation of the *in situ* R_s involved a calculation of the degree of similarity between the actual measured dissipation of PRC data (N_t/N_0) and a calculated dissipation curve using *Eqn 4.1* which can be determined by using the solver function to

estimate a value for *B* which minimises the differences between the two models. The R_s was also calculated in a stepwise manner as detailed below:

1. Calculation of *Log* K_{pw} values for all compounds used in the study;
2. Calculation of PRC responses from extracted sampler sheets;
3. Calculation of the *in situ* sampling rate R_s using Excel programme.

4.4.2.1 Calculation of PRC Responses (N_t/N_0) from Extracted Samplers

PSDs were extracted and cleaned up in accordance with appendix A.6. The results for PRCs in the recovered Lough Bunevella sampler are shown below (*Table 4.6*).

Table 4.6 Concentration of PRCs (ng/g) found after extraction and analysis of the PSD deployed in Lough Bunevella, Co.Mayo in 2009.

Compound ng/g	N_0	Field control	N_t	N_t/N_o	Blank
Naphthalene -$_{d8}$	742	659	28.7	0.04	6.32
Acenaphthene -$_{d10}$	1,506	1,314	92.4	0.06	38.3
Phenanthrene -$_{d10}$	1,964	1,797	307	0.16	19.2
Chrysene-$_{d12}$	2,617	2,788	2,461	0.94	39.8
Perylene -$_{d12}$	4,828	4,869	3,533	0.73	52.5
PCB 29	602	704	327	0.54	n.d
PCB 30	900	950	441	0.49	0.71
PCB 55	1,701	2,163	1,020	0.60	2.22
PCB 78	3,483	4,552	2,060	0.59	n.d
PCB 145	1,679	1,904	996	0.59	9.8
PCB 155	1,589	2,017	990	0.62	n.d
PCB 204	580	858	371	0.64	2.08

n-d – not detected

Once this data had been gathered a second exhaustive extraction of the already processed sheets showed that over 99 % of all compounds had already been extracted hence all future extractions were then completed on a single basis. The field control (used to ensure there was no accumulation from airborne contaminants during

deployment and retrieval) and preparation control results were in close agreement as to the original concentrations of PRCs present in the samplers at the beginning of experiment. Also there appears to be no difference between the concentration (ng/g) of chrysene-d_{12} from the field control and preparation control showing that no photolysis of PAHs had occurred during the exposure. All compounds were inspected to ensure that no co-eluting peaks or interfering matrix effects were present to create any bias of the results. This data was found to be free of analytical interference and was used in the next step for determining the sampling rate (R_s).

4.4.2.2 Calculation of R_s for Lough Bunevella PSD

The estimation of the R_s is effectively a measure of the degree of similarity between the measured dissipation curve as calculated using results found in the previous section (4.4.2.1), and a calculated dissipation curve based on modelled values. The calculated dissipation curve is fitted to the actual curve to estimate the sampling rate that is in closest agreement with the actual PRC dissipation results. This is achieved by firstly dividing the PRC concentration found in the exposed sampler (N_t) by the concentration in the preparation control (N_0). These values are then plotted against the *Log* $K_{pw}M^{0.47}$ which is shown below (*Figure 4.6* A) where *Log* K_{pw} values can be found in *Appendix A.1*. This is the actual dissipation curve. To find out the sampling rate that best fits this curve, the calculated dissipation curve is calculated using the following formula (*Eqn.4.1*);

$$f = \exp\left[-\frac{\mathrm{B\ t}}{\mathrm{k_{pw}M^{0.47}m}}\right] \qquad \text{Eqn.4.1}$$

The data in the column marked Delta (*Table 4.7*) is the value for N_t/N_0 subtracted from the calculated dissipation rate (Calc N_t/N_0) value using *B* which is then summed and squared with the final value labelled as 'Solver' (*Table 4.7*) *i.e.* the value for *B* calculated by the solver programme is that which minimises the difference between calculated and actual dissipation curves. Once the data for the calculated curve (Calc N_t/N_0 *Table 4.7*) are finalised using *Eqn.4.1* the excel solver function is used to find a value for *B*, based on the data in the column marked Delta (*Table 4.7*) which is as close to zero as possible thereby fitting the calculated dissipation curve (*Figure 4.6* B) to the actual dissipation data and calculating the optimal value for *B* which can then be used to calculate the final R_s value using the following formula (*Eqn.4.2*):

$$R_s = \frac{B}{M^{0.47}} \qquad \text{Eqn.4.2}$$

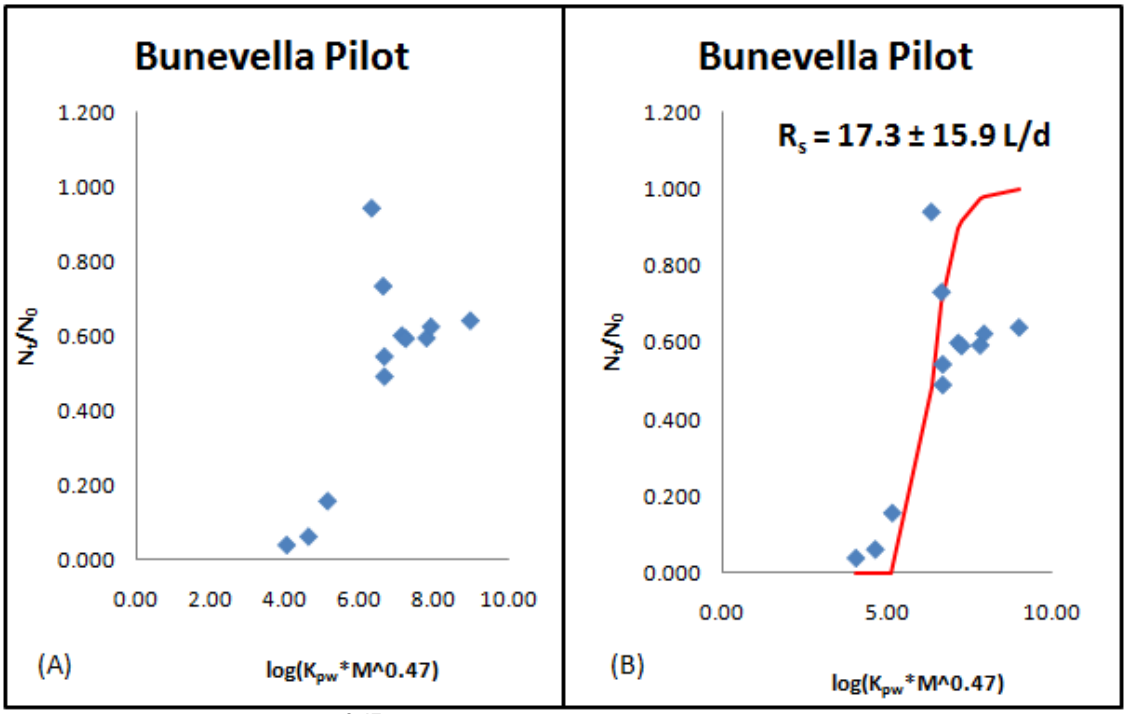


Figure 4.6 *Log (K_{pw}*M^$^{0.47}$)* vs *N_t/N_0* for data on the actual dissipation curve (A) and the calculated curve (B).

This method is known as the unweighted non-linear least squares method (NLS) which has been found to be the best method of estimating the R_s of PDMS passive sampling sheets according to Booij and Smedes.[119] The Excel calculations used here for the estimation of Lough Bunevella R_s are shown (*Table 4.7*) below:

Table 4.7 Excel Programme used to find the optimal R_s (L/d) for the Lough Bunevella sampler using the actual PRC dissipation data and a modelled dissipation calculated using *Eqn 4.1*.

Compound	$log(K_{pw}*M^{0.47})$	N_t/N_0	Calc N_t/N_0	Delta
Naphthalene -$_{d8}$	4.02	0.04	0.00	0.04
Acenaphthene -$_{d8}$	4.61	0.06	0.00	0.06
Phenanthrene -$_{d10}$	5.13	0.16	0.00	0.16
Chrysene -$_{12d}$	6.32	0.94	0.49	0.46
Perylene -$_{d12}$	6.63	0.73	0.70	0.03
PCB 29	6.66	0.54	0.72	-0.18
PCB 30	6.66	0.49	0.72	-0.23
PCB 55	7.14	0.60	0.90	-0.30
PCB 78	7.24	0.59	0.92	-0.33
PCB 145	7.80	0.59	0.98	-0.38
PCB 155	7.92	0.62	0.98	-0.36
PCB 204	8.99	0.64	1.00	-0.36
	B:	253	**Calculated**	
	Solver:	0.92	**R_s L/d:**	17.3
	Deployment duration (d):	110	±	15.92
	Sampler weight (g):	18.5		

This method of estimating the R_s was employed to generate data for all PDMS sheets analysed in this study.

4.4.2.3 Calculating C_w Passive Sampling Dissolved Water Concentrations

Once the data used to calculate the R_s was deemed to be adequate *i.e.* free from analytical interferences, the sampler extracts had internal standard added and were once again analysed on the GC-MS and the GC-ECD respectively, to estimate the concentrations of contaminants found in the sheets. The results calculated for the PAH

and PCB/OC results for sheets from Bunevella are shown (*Table 4.8*) below. Since the second extraction of the sheets for PRCs found only minor traces of analytes those extracts were not further analysed for PAHs and PCB/OCs. The results overall show

Table 4.8 passive sampler concentrations (ng/g) estimated from the analysis of the pilot Bunevella PSD

Compound ng/g	Preparation control	Field control	Bunevella samper	Blank
Naphthalene	53.4	130	18.0	4.60
Acenaphthylene	2.74	2.73	4.47	1.36
Acenaphthene	2.63	2.80	3.72	4.11
Fluorene	5.44	6.11	22.5	1.23
Phenanthrene	10.8	14.5	124	4.50
anthracene	2.74	2.00	15.1	0.81
Fluoranthene	2.63	5.03	212	1.23
Pyrene	5.44	6.19	98.3	1.91
Chrysene	1.40	1.23	22.2	0.69
Benzo(a)anthracene	2.74	2.18	65.4	0.98
Benzo(b)fluoranthene	2.63	2.46	52.0	1.03
Benzo(k)fluoranthene	5.44	2.23	51.4	1.07
Benzo(a)pyrene	1.14	1.78	12.3	0.55
Indeno(1,2,3-cd)pyrene	2.74	2.38	23.2	1.19
Dibenzo(a,h)anthracene	2.63	1.92	11.6	0.82
Benzo(g,h,i)perylene	5.44	2.59	15.6	1.12
HCB	n.d	n.d	2.02	0.05
PCB 18	113	111	22.2	n.d
PCB 31	n.d	n.d	3.74	n.d
PCB 28	n.d	n.d	4.10	n.d
PCB 52	33.8	33.7	14.6	n.d
PCB 44	n.d	n.d	10.2	n.d
PCB 101	81.1	80.8	16.9	n.d
PPDDE	n.d	n.d	6.03	n.d
PCB 149	n.d	0.10	8.28	n.d
PCB 118	n.d	n.d	6.25	n.d
PCB 153	n.d	n.d	18.1	n.d
PCB 105	n.d	n.d	2.22	n.d
PCB 138	n.d	n.d	1.73	n.d
PCB 156	18.3	20.4	2.85	n.d
PCB 180	n.d	n.d	7.60	n.d
PCB 170	n.d	n.d	2.89	n.d
PCB 194	n.d	n.d	4.49	0.13
PCB 209	11.2	14.4	1.79	n.d

n.d – not detected

higher levels of most POPs found in the passive sampler deployed in Bunevella than for those found in the field and preparation controls. Major exceptions were found for in particular naphthalene, phenanthrene and PCBs 18, 52, 101, 156 and 209. In the case of PCBs it was found that the levels in the Field Control were high also. For these contaminants it was decided no further analysis be performed as any result could not be attributed to the passive sampler alone. Calculated PAH concentrations were found to be of good quality and were further used apart from naphthalene which was a compound that was found to be ubiquitous in the laboratory environment, present in all blanks and in high levels in field controls, preparation controls and deployed samplers alike. Monteyne *et al.* [173] also report similar issues for naphthalene speculating that the high fugacity of naphthalene, the exchange rate between air and the PSD is too high to ensure un-contaminated blanks. It was also thought that with this being the first extraction of passive samplers, incorrect adherence to guidelines laid down in the extraction method may be partially at fault and resulted in higher levels found in field and preparation control.

Calculation of the dissolved water concentration of contaminants present is achieved using the following formula (*Eqn* 4.3) as this equation removes the necessity to deciede on the compounds uptake status in regards to equilibrium or kinetic regime:

$$C_w = \frac{N_t}{K_{pw} m \left[1 - \exp\left[-\frac{Bt}{K_{pw} M^{0.47} m}\right]\right]} \qquad \text{Eqn.4.3}$$

The N_t in this case is the concentration (ng/g) found in the exposed passive sampler analysed in the previous section. Where there were high masses of contaminants found

in the blanks these were subtracted from the levels found in the samplers and this result was used to calculate the C_w, in one case (acenaphthene) this resulted in no value being calculated. Results for PAHs and PCBs/OCs from Lough Bunevella are shown (*Table 4.9*) below. The results generated using *Eqn. 4.3* are given in pg/L which indicates that the passive sampling device is analytically sensitive, but for convenience results are presented in ng/L.

Table 4.9 Passive sampling derived dissolved water concentrations (ng/L) of Bunevella PSD.

Compound	Result ng/L	Compound	Result ng/L
Acenaphthylene	1.71	PCB 31	0.04
Acenaphthene	n.d	PCB 28	0.04
Flourene	3.45	PCB 44	0.11
Phenanthrene	9.25	PPDDE	0.06
anthracene	0.88	PCB 149	0.09
Flouranthene	5.34	PCB 118	0.06
Pyrene	2.18	PCB 153	0.19
Chrysene	0.25	PCB 105	0.02
Benzo(a)anthracene	0.73	PCB 138	0.02
Benzo(b)flouranthene	0.50	PCB 180	0.08
Benzo(k)flouranthene	0.50	PCB 170	0.03
Benzo(a)pyrene	0.12	PCB 194	0.05
Indeno(1,2,3-cd)pyrene	0.21	HCB	0.03
Dibenzo(a,h)anthracene	0.10		
Benzo(g,h,i)perylene	0.14		
∑PAH	25.4	∑PCB/OC	0.86

n.d – not detected

As can be seen from results presented (*Table 4.9*) above the levels of contaminants (ng/L) in Lough Bunevella are low overall. The PAHs are higher than the levels of PCBs and OCs with the ∑PAHs concentration measuring 25.4 ng/L, while the ∑PCBs+OCs measured 0.86 ng/L. Of the PAHs found major contributions were noted for phenanthrene, fluoranthene, fluorene and pyrene and of the PCB/OC major contributions were notes for PCB 153, 149 and 44. As this pilot study was primarily used in the familiarisation of passive sampler technology this data was not used beyond

this purpose. The calculation of the Bunevella pilot sampler was considered complete, calculations of other devices deployed in the area are discussed below.

4.4.3 Calculation of C_w from PSDs Deployed in the Burrishoole Catchment

With the improvements in passive sampler analysis and lessons learned from the pilot study complete the calculation of C_w from passive samplers deployed in the Burrishoole catchment area of Co. Mayo proceeded using the procedure outlined in the previous section (section 4.4.1). This included the calculation of the masses of PRCs found in the samplers deployed (N_t) compared to the field and preparation controls (N_0). This data is then used to calculate the R_s and finally the C_w for all compounds found in the region.

4.4.3.1 Calculation of R_s for Burrishoole PSDs

Passive sampling devices were deployed in the Burrishoole region at the sites shown in *Fig 4.2* and *Table 4.1* at the same time as the pilot Bunevella sampler was being retrieved. While the pilot Lough Bunevella sampler was left *in situ* for 110 days the subsequent passive samplers were deployed for only 60 days. This time period is more representative of typical passive sampler deployment. Calculation of the R_s took place in a similar manner as outlined in section 4.4.2.2 with results shown in *Fig 4.7*. Data used to generate these results is shown in appendix A.7. The passive sampler at the Black River has the highest R_s at 24.8 L/d while Gallaghers Lake has the lowest R_s values at 3.2 L/d. The Black River site was at the northern part of Lough Feeagh at a confluence of two rivers (Black and Glenamong Rivers), which was a very turbulent part of the lake with deep fast moving water, hence a high R_s value could be expected here. Gallaghers Lake is isolated with one underground river feeding the lake hence there is slow moving shallow water at this location which would mean a lower R_s value

for the passive sampler. The sites at Lough Bunevella and eel Weir were both in more sedate locations in comparison with the Mill race (Black River) regarding the movement of water. This is also reflected in the calculated R_s values.

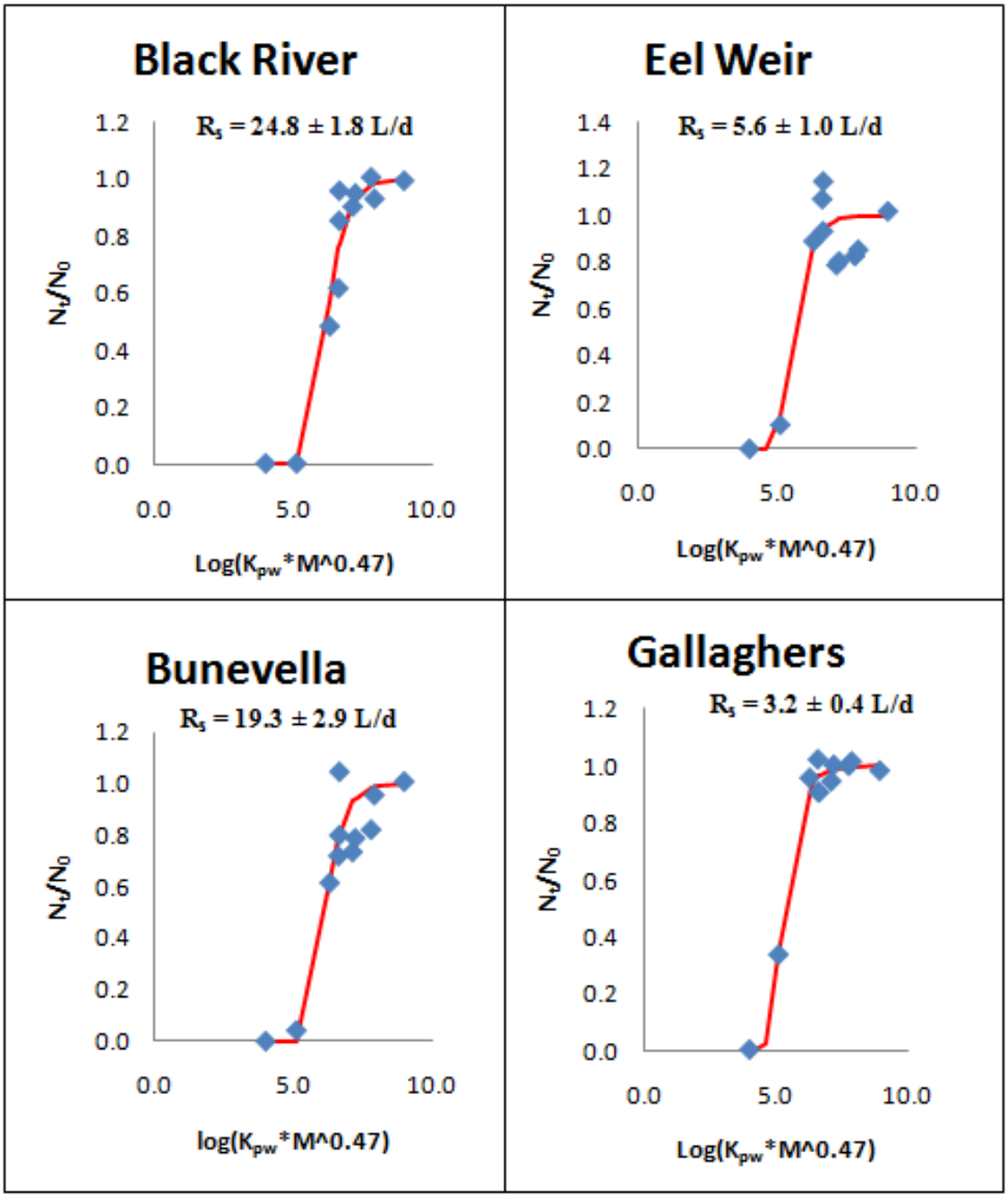


Figure 4.7 Sampling rate estimation (L/d) for all passive samplers from the Burrishoole catchment, The higher R_s found at the Black River site inticates a more turbulent area.

4.4.3.2 Calculation of C_w for Burrishoole PSDs

The calculation of passive sampler derived dissolve water concentrations (C_w) took place in accordance with section 4.4.2.3 with the concentration results shown in appendix A.7. Passive sampler extracts were analysed for POPs of interest using the GC-ECD for PCBs/OCs and on the GC-MS for PAHs. In the case of this extraction of PSDs, since there was a larger amount of data produced, a check on the suitability of the concentrations of analytes generated in relation to LOD was performed in accordance with section 3.5.2.3. Briefly, a compound's concentration was deemed a valid result if it was greater than three times a blank (3 x blank) value or if there was no corresponding peak in a T_0 sampler. Once these rules were applied it was possible to calculate C_w values using *Eqn 4.3*. *Table 4.10* below shows the C_w values calculated for PAHs/PCBs and OCs.

PAHs ranged from 0.06 ng/L for dibenzo(a,h)anthracene and benzo(g,h,i)perylene in the Black River sampler to 16.6 ng/L for phenanthrene at the eel Weir site. There are again major contributions from phenanthrene (31.5% total PAH contribution) fluoranthene (16 %), flourene (13.9 %), acenaphthylene (11.9 %) and pyrene (9.7 %) to the total PAH concentration found (∑PAHs). These compare well with the previous Lough Bunevella pilot sampler where major contributions were also seen for phenanthrene (36.5% total PAH contribution) fluoranthene (31 %), fluorene (13.6 %), acenaphthylene (6.73 %) and pyrene (8.58 %). Results reported by O'Hara [123] in marine waters showed major contributions from phenanthrene (20.9 %), Fluoranthene (14 %) and pyrene (13.5%) which again compares well with this study. Overall these PAH compounds represented an average of 83 % of the ∑PAHs which compares well to a study by Schafer *et al.* [174] where it is reported that phenanthrene, pyrene and fluoranthene contribute an average of 91 % to the total PAH concentration present.

Table 4.10 PAH/PCB and OC C_w (ng/L) for samplers deployed in the Burrishoole catchment

Compound (ng/L)	Black River (BR)	Eel Weir (EW)	Bunevella (LB)	Gallaghers (GL)
Acenaphthylene	5.28	4.36	3.93	5.14
Acenaphthene	1.71	1.22	1.29	1.85
Fluorene	4.51	5.86	5.30	7.26
Phenanthrene	10.2	16.6	14.1	13.0
Anthracene	0.31	0.80	0.19	0.31
Fluoranthene	3.06	15.6	9.6	3.72
Pyrene	1.71	8.84	6.05	2.56
Chrysene	0.14	1.23	1.12	0.30
Benzo(a)anthracene	0.38	4.86	3.23	0.92
Benzo(b)fluoranthene	0.14	3.28	1.65	0.29
Benzo(k)fluoranthene	0.13	2.16	1.16	0.26
Benzo(a)pyrene	0.06	0.49	0.35	0.16
Indeno(1,2,3-cd)pyrene	0.09	0.89	0.48	0.22
Dibenzo(a,h)anthracene	0.06	0.30	0.16	0.13
Benzo(g,h,i)perylene	0.06	0.58	0.35	0.23
HCB	0.03	0.05	0.52	0.05
PCB 28	0.02	0.10	4.40	1.71
PPDDE	0.06	0.24	5.58	1.59
PCB 149	0.01	0.04	0.20	0.20
PCB 118	0.08	0.31	5.96	2.81
PCB 153	0.11	0.54	8.83	3.58
PCB 105	0.04	0.09	2.55	0.66
PCB 138	0.06	0.45	7.65	3.40
PCB 180	0.04	0.15	1.91	1.74
α-HCH	3.32	2.91	2.36	0.66
β-HCH	3.40	2.09	3.11	0.01
op-DDT	0.20	1.12	0.65	0.54
pp-DDT	0.20	0.94	0.31	0.10
Transchlordane	0.04	0.09	0.13	0.11
Heptachlor epoxide	0.14	0.22	0.14	0.17
∑PAH	27.8	67.1	49.0	36.3
∑PCB+OC	7.75	9.34	44.3	17.3
Total ∑PAH + ∑PCB + OC	35.6	76.4	93.3	53.7

PAHs contribute on average of 72 % to the total concentration of contaminants measured (∑PAH + ∑PCB + OC as per *Table 4.10*) at the Burrishoole catchment however at two of the sites (Bunevella L. and Gallaghers Lake) the levels of both

compounds is more evenly spread (average of 60 % - 40 % respectively). PCBs ranged from 0.01 ng/L for PCB 149 at the Black River location to 8.83 pg/L for PCB 153 at Bunevella while the OCs ranged from 3.4 ng/L for β-HCH to 0.04 ng/L for *trans*-chlordane at the Black River site. There were major contributions from PCB 153, 138, 180 and 118 and OCs α-HCH and β-HCH. The two Lough Feeagh sites (Black River and eel Weir) have similar profiles but the more turbulent site at Black River with fast moving water has a lower ∑PAH + ∑PCB + OC at 35.6 ng/L compared to 76.4 ng/L at the eel Weir. Lough Bunevella had the highest ∑PAH + ∑PCB + OC at 93.3 ng/L and a different profile to that of the Lough Feeagh sites in that PCB/OCs fraction contributed almost 50 % of the total ∑PAH + ∑PCB + OC concentration present. Gallaghers Lake had a similar profile to that of Bunevella in that the PCB/OC fraction contributed 32.3 %. This may indicate that Lough Feeagh, from a contaminant influence point of view, is much different to. Bunevella L. and Gallaghers Lake.

4.4.3.3 Analysis of PCP using passive samplers in the Burrishoole

The use of PSDs to screen for PCP (pentachlorophenol) in the Burrishoole resulted in no detection of PCP. The Log K_{ow} for PCP according to Mackay [175] is 5.18 meaning that PCP is hydrophobic and as such should be a prime candidate for accumulation by PDMS passive sampling devices, however many studies report that PCP is photo-mineralised by sunlight within a few days.[76] Hence if any contamination event in the region was a historical one then PCP would not be present in the passive sampling devices used in the region. PCP can be adsorbed to suspended particulate matter where it will be locked in sediment and further degraded microbiologically. If PCP is the source of contamination in the Burrishoole catchment, PSDs (which samples the freely dissolve water concentration) may not be able to accumulate the contaminant to any great degree. Some reports suggest that a major breakdown product of pentachlorophenol may be pentacholoranisole (PClA) which may also be classed as a POP.[78] Further, analysis was completed for PClA however PCP/PClA was not detected in the screening of PDMS extracts.

While PCP or PClA was not detected the focus of the study moved towards the analysis of PCDD/F residues as a proxy indicator for PCP itself. Analysis of passive sampling devices and a final sediment composite sample for PCDD/Fs was completed by Eurofins Gmbh in Germany. Sediment results are shown in section 4.3.1.2 while passive sampler results are shown below (section 4.4.3.4)

4.4.3.4 Analysis of PCDD/Fs in PSDs

PCDD/Fs analysis was completed on passive sampler extracts (per sampler basis) from the Burrishoole with the results (ng/sampler) shown in (*Table 4.11*) below. Results shown are based on the actual concentration found in the sampler when analysed (ng/sampler) as there are currently no co-solvent method derived *Log* K_{pw} values reported for PCDD/F hence there can be no accurate calculation of C_w values. The results for the sum of PCDD/F (∑PCDD/F) found in the passive samplers ranged from 22.6 ng/sampler at the Omey Island control site (site H *fig 4.2*) up to 278 ng/sampler at the Black River site.

The results for the sum of PCDD/F (∑PCDD/F) for two sites in the Burrishoole (Black River and eel Weir) were elevated in comparison to the other sites both inside and outside the Burrishoole catchment. This being consistent with the PCDD/F eel results reported by McHugh *et al.* [153] where eels from outside the Burrishoole showed a lower level of PCDD/F than those from inside the region. The ratio (%) of ∑PCDD to the total ∑PCDD/F concentrations found in the sampler were telling in that for the two elevated sites (Black River and eel Weir) ∑PCDDs account for 92.4 % at both locations while the ∑PCDFs account for 7.6 %. This is slightly different at Lough Bunevella where ∑PCDDs account for 75.3 % and 45.5 % at Gallagher s Lake

Table 4.11 PCDD/F upper-bound concentrations (ng/sampler) for all PDMS passive samplers analysed in the Burrishoole region plus two extras from outside the region for comparison (Cork and Omey Island) (Codes included for inclusion in *Fig* 4.9)

Compound (ng/sampler)	Black River	Eel Wier	Bunevella	Gallaghers	Cork	Omey Island
Code	BR(PDMS)	EW(PDMS)	BU(PDMS)	GL(PDMS	CK(PDMS)	OIPDMS
2,3,7,8-TetraCDD	0.36	0.36	0.36	0.36	0.36	0.36
1,2,3,7,8-pentaCDD	0.89	0.92	0.71	0.97	1.08	0.50
1,2,3,4,7,8-hexaCDD	0.99	0.98	0.96	0.96	0.96	0.96
1,2,3,6,7,8-hexaCDD	0.98	1.07	0.96	0.96	0.96	0.96
1,2,3,7,8,9-hexaCDD	0.96	0.96	0.96	0.96	0.96	0.96
1,2,3,4,6,7,8-heptaCDD	17.7	18.7	4.89	4.33	3.44	1.66
OctaCDD	235	208	34.9	15.7	9.5	5.80
2,3,7,8-TetraCDF	0.64	0.64	0.64	0.64	0.77	0.64
1,2,3,7,8-pentaCDF	0.86	0.86	0.86	0.86	0.86	0.86
2,3,4,7,8-pentaCDF	0.86	0.86	0.86	0.86	0.86	0.86
1,2,3,4,7,8-HexaCDF	0.80	0.80	0.80	0.80	0.80	0.80
1,2,3,6,7,8-HexaCDF	0.80	0.80	0.80	0.80	0.80	0.80
1,2,3,7,8,9-HexaCDF	0.80	0.80	0.80	0.80	0.80	0.80
2,3,4,6,7,8-HexaCDF	0.80	n.d	0.80	0.80	0.80	0.80
1,2,3,4,6,7,8-HeptaCDF	1.20	1.05	0.76	1.80	1.64	0.76
1,2,3,4,7,8,9-HeptaCDF	0.76	0.76	0.76	0.76	0.76	0.76
OctaCDF	13.6	12.3	7.27	20.9	31.6	4.28
∑PCDD	257	231	43.7	24.2	17.3	11.2
∑PCDF	21.1	18.9	14.4	29.0	39.7	11.4
∑PCDD + F	278	250	58.1	53.3	57.0	22.6

n.d – not detected

The two samples from outside the area (Cork and Omey Island) are different again in that the ∑PCDDs accounts for 30.3 and 49.6 % of the total ∑PCDD/F respectively. This would indicate that at the Lough Feeagh and perhaps the Lough Bunevella site the PCDD/F profile is very different to Gallaghers Lake in the Burrishoole region and to the other samples from outside the region.

The congener profile is again dominated by the OCDD congener at the Black River and eel Weir sites where this compound contributed 84.5 and 83.2 % respectively to the

∑PCDD/F concentrations (ng/sampler) found. This compares well with the eel and trout samples from this study and those from Mc Hugh *et al.* [153] where the ∑PCDD/F was dominated by the OCDD congener. For the rest of the sites the OCDD congener is not as dominant ranging from 60.1 % at Lough Bunevella to 16.7 % of the ∑PCDD/F at the Cork site. A percentage congener contribution table (*Fig 4.8*) below for the Lough Feeagh sites (Black River and eel Weir) shows a profile similar to that found in the eels (*Fig 4.3*) and sediment (*Fig 4.5*) from Burrishoole. This indicates that the dioxin profile present in the eel, trout and sediment samples is also present in the water column in the Lough Feeagh sites (Black River and eel Weir) and possibly in the Lough Bunevella site also. The PCDD/F profile shown in *Fig 4.8* strongly resembles that the PCDD/F found in technical PCP (reproduced from Birch *et al.* [164] *fig 4.3*). The profile present in the other samplers is distinctly different to those found for the Lough Feeagh sites (Black River and eel Weir) apart from Lough Bunevella, and data supports the hypothesis that there may be a point source input to the lake.

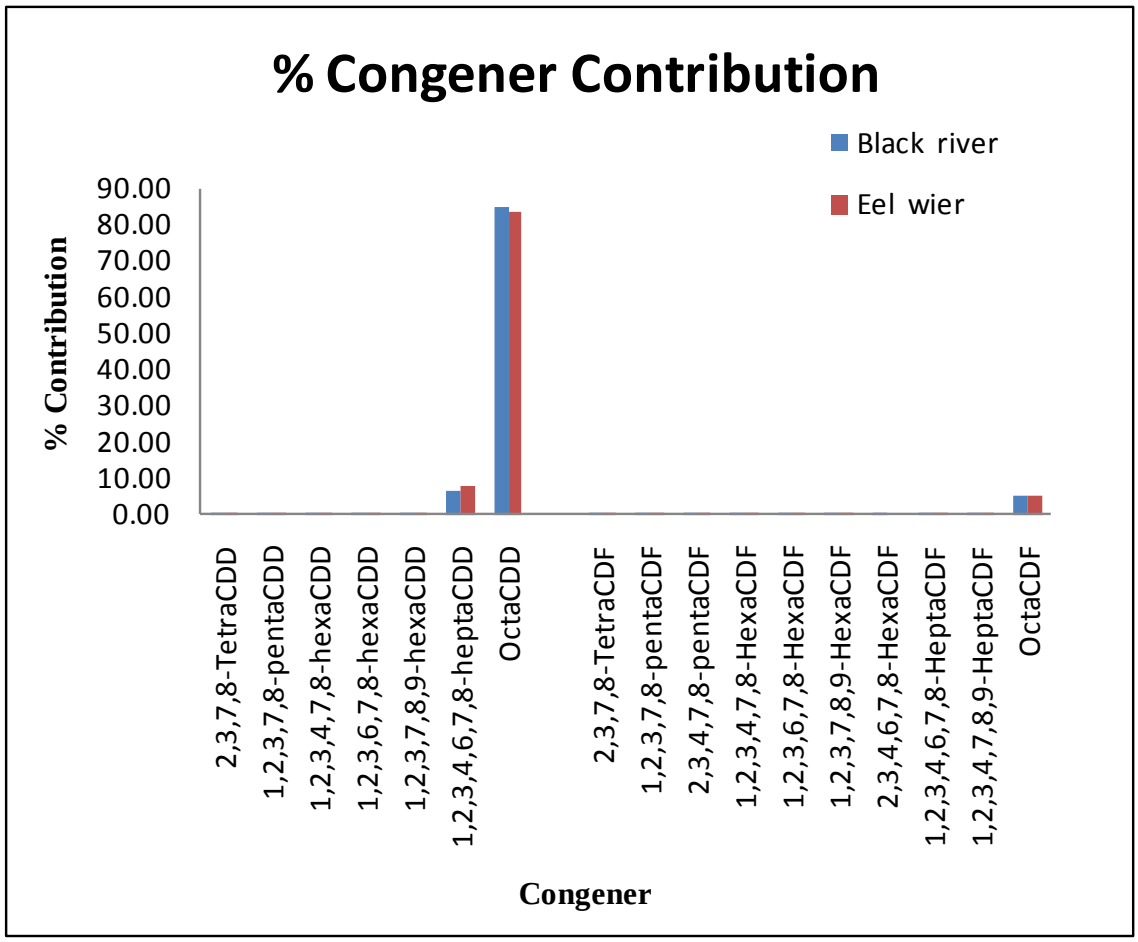


Figure 4.8 PCDD/F % congener contribution from Burrishoole PDMS samples

All data generated as part of this study in biota, sediment and passive samplers is further shown in appendix A.7 *Tables 4* and 5.

4.4.3.5 Conclusion for PSDs in the Burrishoole Catchment

The use of PDMS passive samplers in the Burrishoole catchment was considered to have been a successful exercise for both screening and analytical purposes. The preparation of the samplers, deployment/retrieval and ultimately analysis provided invaluable insights into the strengths and weaknesses of the passive sampler design. The clean up and spiking of the sheets is straight forward. Their storage and deployment is likewise straight forward. All samplers deployed were successfully returned indicating that the system is suitable for sampling prolonged periods (up to 4 months) in the environment. The suite of analytes with estimated C_w values reported ranged from

PAHs to PCBs/OCs. PSDs can be expected to cover a high percentage of compounds required for legislative directives including the WFD (further discussed in chapter 7). Analytically the passive sampler extracts provided higher levels of contaminants than might be found in a traditional water sample which makes the sensitivity required more easily attained and with the use of targeted PRCs to ascertain the amount of water sampled over the deployment period, the passive sampler system proved to be a very useful tool with which to improve integrative environmental monitoring.

The *Log* K_{pw} values required to estimate C_w for PCDD/F compounds are not currently available but will no doubt be available in the future which broadens the suite of analytes for passive samplers. To this author's knowledge there are currently very few, or no papers in the literature regarding the use of PDMS PSDs to estimate C_w values for PCDD/F compounds in the marine environment however results presented here show that these devices can be used to screen for these compounds. The lessons learned during this study can now be applied to the use of passive samplers in other locations.

4.5 Pollution Sources and Congener Patterns Using PCA

Dioxins may originate from a wide range of industrial point and/or diffuse sources. Source tracing studies using a low number of congeners have in the past been used to indicate that atmospheric deposition is a major contributor to total PCDD/F fluxes to Baltic Sea water. Armitage *et al.* [176] and Masunaga *et al.* [172] further showed that comprehensive congener patterns have significantly higher potential for identifying sources than just 2,3,7,8-substituted PCDD/F patterns or homologue profiles, thus multi-congener based principal components analysis (PCA) is a beneficial technique when attempting to elucidate the origins of PCDD/Fs compounds in the Baltic Sea.

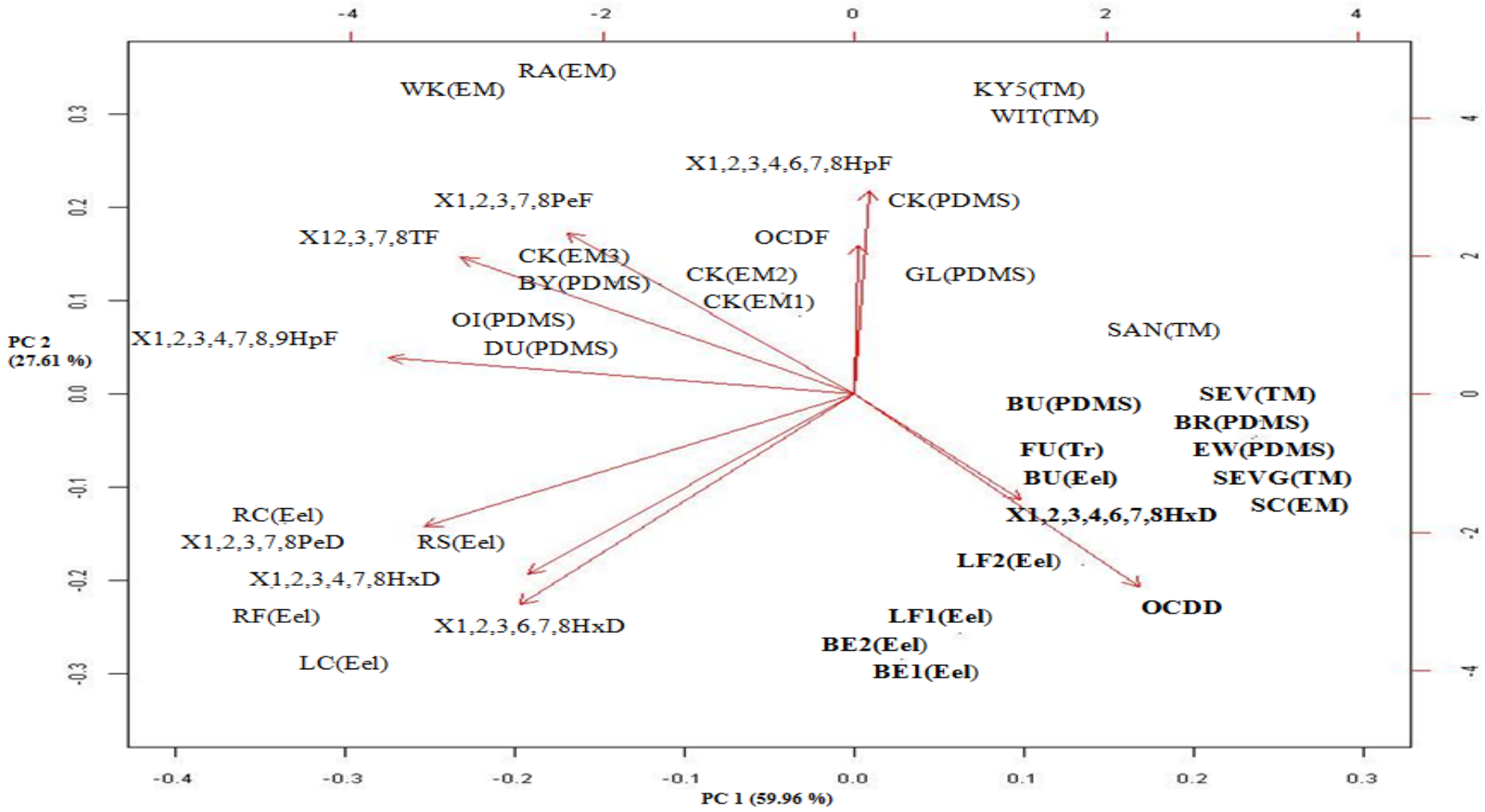
PCA, introduced by Pearson in 1901,[177] is a mathematical procedure which can be used to reduce a set of possibly correlated variables into a set of uncorrelated linear variables called principal components. For PCA, PCDD/F concentration data were scaled to unit variance/normalised, thereby all variables have equal weighting. If such scaling is not performed, variables with high nominal value/concentration will dominate and outweigh any important information in variables of lower nominal value. This technique enabled concentration-independent congener profiles at test sites and between matrices to be compared to potential sources and minimised the potential influence of concentration-based noise effects (*e.g.* LOQ) on PCA output. This normalisation process was completed relative to the sum of a number of individual congeners (n=10) that were measured in all samples and in prospective source samples including profiles from diverse combustion-related flue gas samples (n = 6 Irish locations) and PCDD/F concentrations reported by Sundqvist *et al.* [66] for PCP and TeCP technical mixtures (n=5) which were evaluated against profiles in biota, PDMS and sediment from the Burrishoole region and in other Irish samples with results shown in *Figure 4.9* with information used to generate this plot shown in appendix A.7 *Table 4* and *5* and *Table 4.11*.

PCA of samples was restricted to three significant principal components (PCs). The first two PCs (PC1 and PC2) were found to explain >87% of the variation in the data (60 and 27.6 %, respectively). Vector loading plots suggest that the ordinance of Burrishoole samples is strongly influenced by OCDD and 1,2,3,4,6,7,8-HeptaCDD. Greater proportions of OCDD and 1,2,3,4,6,7,8-HeptaCDD in environmental samples have been suggested to be due to the sources originating from chlorophenol related inputs [172] while greater proportions of TCDFs suggest sources originating from PCB mixtures, chlorobenzenes, chlor-alkali process, or the incineration of PCBs and PVC. Geeraerts *et*

al. [162] further showed a variety of dioxin profiles in eels from Belgium suggesting that the dioxin profile found in the animals was dependent on local input sources.

It is additionally evident that the profile (*Figure 4.9*) strongly resembles that derived from a number of candidate sources, namely that of the PCP technical mixture Sevarex and TeCP technical mixture Sevarex granulate. It should be noted that while this study utilises literature derived PCDD/F concentrations in named PCP and TeCP technical mixtures, that other similarly produced mixtures would be expected to exhibit similar chromatographic profiles. Profiles reported for other technical mixtures (TeCP/PCP mixtures RA and WK) were found to be less similar. Air emissions data from sample SC(EM) show a similar profile to that observed in the Burrishoole samples. This sample was derived from a former wood chip production facility located in Scariff Co Clare, >150Km south East of the Burrishoole catchment. The prevailing wind direction in the West coast of Ireland is between west and south thus historic emissions from this plant would not be expected to greatly influence the profile obtained in Burrishoole samples. To further support this, eels sampled from Lough Corrib located mid way between Burrishoole and Scariff do not exhibit the same higher chlorinated PCDD profile.

Figure 4.9 Principal components analysis bi-plot for selected PCDD/F congeners (n=10). Generated from contribution of individual PCDD/F congeners to the Σ10PCDD/F in sediment, passive samplers (PS), air emissions (AE)(EPA monitoring), biota (eel and trout) and technical tetra and pentachlorophenol mixtures.[66]



As previously discussed, total concentrations of PCBs in Burrishoole samples were comparable to those in samples from the rest of Ireland suggesting that PCBs are unlikely to be a source of the PCDD/PCDF profile. Other sources such as chlorophenol and chlorobenzene production, incineration related activities, and/or chlor-alkali processes are often associated with changes in PCDD/F profiles however given the remote location of the site and the absence of intensive industrial activity these are not expected to contribute greatly to the PCDD/PCDF profile.

Overall while PCP itself was not detected in test samples the profile of relative concentrations of PCDD/PCDF congeners in biota, PDMS and sediment collected from the Burrishoole area when compared with samples collected from other locations strongly suggests historic local use of a PCDD containing substance or product within this catchment.

4.6 Conclusion

The Burrishoole catchment proved to be a very interesting area in which to perform analysis of environmental matrices. This isolated site provided tough challenges both logistically and analytically in relation to sampling and analysis. The levels of PAHs and PCBs found are low in comparison to other sites indicating low level anthropogenic input in the Burrishoole region however the elevated PCDD/F levels found in the catchment from analysis of biological tissue, sediment and passive samplers indicate that a point source may be or have been present. PCA PCDD/F profiles suggests a chlorophenol based input and in particular that of PCP as a possible influence in this location. To this author's knowledge there are no industrial or agricultural sources at present, or in the past which could explain this profile. There are however strong

literature links between PCP production and high levels of PCDD/F as bi-products. Literature derived PCDD/F and HO-PCDE profiles in technical PCP mixtures suggest that PCDD/F and HO-PCDE profiles as measured in PDMS from the Burrishoole region (apart from Gallaghers Lake) better ressembles that of PCP formulations than do profiles from other Irish locations. Future investigative work is warranted which should concentrate on the local indigenous marine wildlife, sediment and water either through passive sampling or traditional water sampling techniques. To aid the detection and determination of a possible point source in the Burrishoole catchment an expansion of sampling matrices should be included such as soil samples from around Lough Feeagh in conjunction with samples of wood from the surrounding forests.

The first use of passive samplers in the catchment to estimate concentrations of dissolved water borne contaminants has proven to be a learning experience. There are many questions which this study has answered. Passive samplers, properly operated, can be used as a valuable tool for environmental monitoring. The system itself is robust in the environment. Extraction and analysis provide excellent sensitivity analytically and the range of compounds analysed is growing all the time.

Chapter 5: Passive Samplers: A Role in Pollutant Monitoring in Continental Shelf Waters?

5.1 Introduction

Ireland lies within the approximate geographical **latitudes** of 51.5 to 55^{o} N and **longitude** of between 6 to 10^{o} W and is bounded by the continental shelf which runs along the edge of the island, from a south west to north east direction. The deeper waters immediately to the west of Ireland are thus subjected to a variety of oceanic influences including the Gulf Stream, sub-Arctic intermediate waters (SAIW), North Atlantic deep water (NEADW) and Mediterranean (MW) influences, each of which contain different chemical "signals" (salinity, nutrients *etc*) that can be used for source attribution purposes.[178] Since these water masses occur at broadly different depths and are each of different origin it would not be unexpected that each water mass may exhibit different anthropogenic contaminant profiles. These patterns may be attributable to previous agriculture and/or industrial influences with pollutant loadings entering the ocean through rivers, rainfall and atmospheric deposition.[178,179]

The M6 weather buoy is part of a wider Irish Weather Buoy Network and is located on the 53^{o} N line of latitude at a distance of approximately 400 miles off the West coast of Ireland in waters down to approximately 3000 metres depth (see *Fig 5.1*). The M6 platform is utilised to routinely house instrumentation for the measurement of weather parameters (*e.g.* pressure, wave height *etc*) in addition to the measurement of conductivity, salinity and flow rates via MiniCat CTD devices present on the mooring rope at approximately 5 m, 250 m, 500 m, 750 m and 1040 m.

The primary purposes of this chapter are to document for the first time in Irish waters, the deployment of passive sampling devices in this dynamic environment and to assess the applicability of passive sampling in monitoring offshore waters, this assessment was completed in a stepwise manner as follows;

a) Reporting of the measurement of time averaged PSD derived persistent pollutant loadings dissolved pollutants levels (PAH, PCBs and OCs) in deep Atlantic waters using both SPMD and PDMS,
b) Discussion of the comparative performance (specifically the applicability of both PDMS and SPMD devices for PAH and PCB groupings),
c) Comparison of modelled data to literature from deep-sea environments,
d) Completion of a statistical assessment of pollutant profiles at depths ranging from surface (5 m) to 1040 m,
e) Overall discussion and recommendation regarding the relevance, applicability and the advantages and disadvantages of passive sampling in off shore environments.

5.1.1 Environmental Description of M6

The M6 weather buoy (53.07482°N, 15.88135°W) is located above the Rockall Trough which is a deep-sea channel located to the west of the Irish continental shelf bounded by the Rockall Bank (*Fig 5.1*). Located to the west of the Rockall Trough, lies the boundary between two counter rotating gyres, namely the sub-polar and sub-tropical gyres.

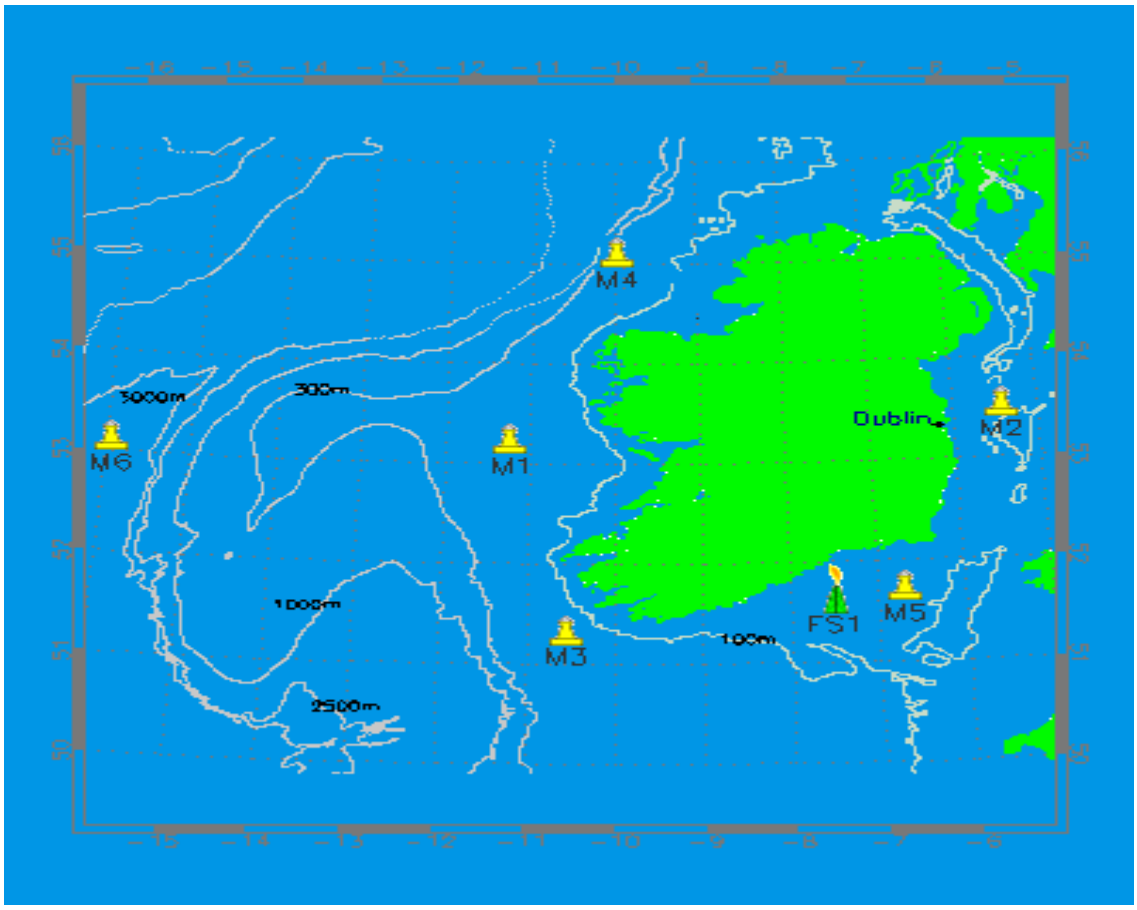


Figure 5.1 Location of the M6 weather buoy approximately 400 miles off the West coast of Ireland, directly over the Rockall Trough which has a water depth of 3000 meters.

The Rockall Trough has attracted scientific interest over many decades as a pathway for heat and freshwater transport from the North-eastern Atlantic to the Nordic Seas.[179] The Trough is about 3500m deep at the southern opening, and is bounded to the east by the continental shelves of Ireland and Scotland. The northern end of the trough is separated from the Faroe Bank and Faroe-Scotland Channels by the 500 m deep Wyville-Thomson overflow ridge.[180] The eastward flowing North Atlantic Current (NAC), an extension of the Gulf Stream, divides when it meets the Rockall Plateau with one branch flowing northward, west of Rockall Plateau towards Iceland, while another enters the Rockall Trough where it meets the eastern boundary current of the European continental margin.[179,181]

5.1.2 Passive Sampler Preparation, Deployment and Retrieval

The SPMD and PDMS samplers were both prepared and spiked in accordance with literature guidelines [117,115] SPMD PSDs were prepared and spiked in October 2008 at the Royal Netherlands Institute for Sea Research (NIOZ) and transported, with deployment cages, to the Marine Institute laboratories where they were frozen awaiting deployment. The PDMS PSDs were prepared and spiked at Fisheries Research Services (now Marine Scotland), Aberdeen, in January 2009.

Figure 5.2 The SPMD and PDMS Cage containing the samplers which was covered in aluminium to protect against air borne particles/contamination during deployment.

The PDMS and SPMDs were firstly attached to the deployment cages (*Figure 5.2*) and covered with aluminium foil for transport purposes. Five cages containing 2 of each type of sampler (deployment details in *Table 5.1*) were successfully deployed in August 2009 at the M6 site. Cages were deployed in tandem with physico-chemical monitoring (MiniCat) devices previously discussed. Each cage contained 12 PDMS sheets to provide 2 samplers (6 sheets = 1 sampler) and 2 SPMDs to sample the water column at

each selected depth. Due to a number of issues outside of the control of the project samplers were only retrieved in May 2011 after 585 days at sea, whereupon they were returned to the Marine Institute laboratories and frozen prior to extraction and analysis.

The deployment duration at the M6 site challenged previous passive sampling literature in that the length of time deployed (585 days) is beyond the scope of previous sampler deployments. *Table 5.1* details the number of retrieved samplers from the M6 site. The majority of PDMS samplers deployed were lost (83 %) while SPMDs survived the deployment better with 40% of the samplers lost. The cage at 500 m containing all the samplers was also lost. Other cages were returned fully intact however a number of the samplers were absent. Rationale for the high attrition rate are unclear however it is thought that a combination of the long deployment period and the dynamic nature of environment may be factors in the high losses.

Table 5.1: Number of SPMD and PDMS PSDs deployed (and in parenthesis successfully returned) from the M6 weather buoy in May 2011

	Sampling depth (m)				
	5	**250**	**500**	**750**	**1040**
PDMS	12 (1)	12 (3)	Cage lost	12 (3)	12 (6)
SPMD	2 (0)	2 (2)	Cage lost	2 (2)	2 (2)

5.2 Extraction and Analysis of PDMS PSDs

PDMS PSDs recovered from the M6 weather buoy were extracted as per methods detailed in chapter 3 and analysed as previously discussed in chapter 4. Briefly, the calculation of C_w values for the PDMS samplers deployed and retrieved at M6 requires a number of stepwise elements:

1. Calculation of responses for PRCs found in field control, preparation controls and in exposed samplers, and the calculation of *in-situ* sampling rates (R_s),
2. Calculation of concentrations (ng/g) in the PSDs, including quality control information,
3. Estimation of C_w (ng/L) concentrations from PSDs.

As differing numbers of PDMS sheets were available for analysis, final modelled concentration data were calculated relative to the number of PDMS sheets available.

5.2.1 Calculation of Depth Specific R_s Values at M6

Calculation of the R_s for PDMS is described in section 4.4.2 and so is not further discussed here. Final sampling rates (R_s) and fitted curves for PDMS are detailed in *Fig 5.3* with the data used shown in appendix A.8 *Tables 1 - 3*. It should be noted that given the extended deployment period the deuterated PAHs used as PRCs for the lower *Log* K_{pw}^{so} values were completely depleted in most cases which is not surprising given the length of the deployment. The lower *Log* K_{pw} PCBs used as PRCs were similarly depleted apart from the higher molecular weight compounds (PCB 145, 155 and 209) with between 40 – 60 % depletion evident for these compounds. *Figure 5.3* illustrates that the calculated R_s values using the data shown in appendix A.8, for the samplers at

depths 5 and 250 m (40 and 44.6 L/d) are similar while the samplers at 750 and 1040 m are also similar (150 and 125 L/d) and very different to the samplers at the upper depths. These calculated R_s values were deemed to be sufficient for the calculation of C_w values as per section 4.4.2.3.

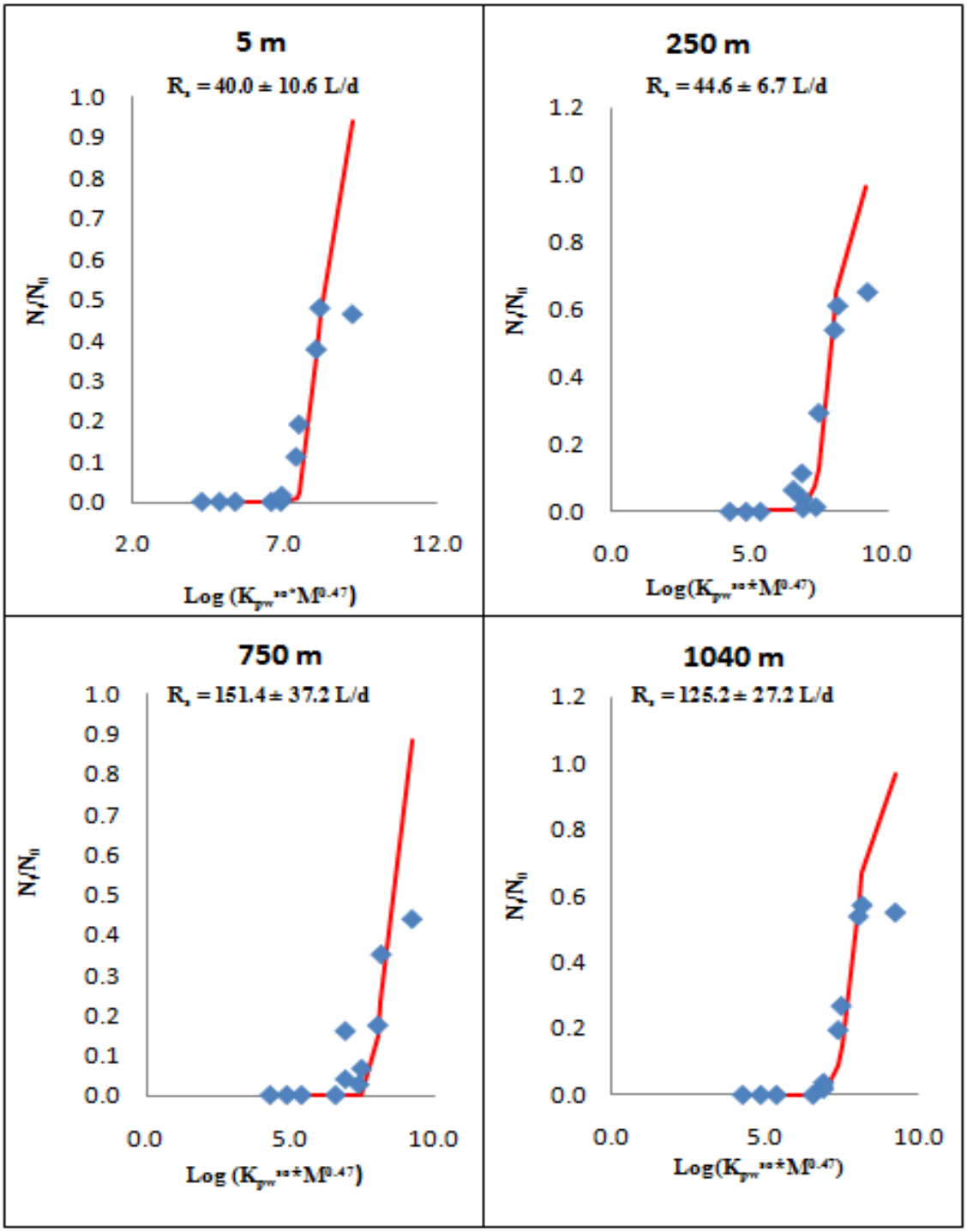


Figure 5.3 Estimated PDMS R_s values for the 4 sampling depths at the M6 weather buoy

5.2.2 Results and discussion

This section details both physico-chemical and analytical data generated to support identification of putative water masses and consequently potential contaminant loading influences in addition to documenting a range of techniques used to calculate dissolved water concentrations of key pollutants, to evaluate the performance of the different PSDs at depth and to compare derived concentration data to key threshold values. This section is broken down into the following components in order to achieve this.

a) Instrumental and experimental physico-chemical parameter measurement of Rockall water masses,
b) Separate assessments of PDMS and SPMD passive samplers,
c) Performance and comparison of modelled SPMD and PDMS Data.

5.2.2.1 Measurement of Physico-chemical Parameters in Rockall Water Masses.

Flow meters, positioned on the M6 weather buoy at all depths (summary data in appendix A.8 Table 4) indicate that the prevailing current ~ 80 % of the time is from 60 to 210 degrees which corresponds to water from a south east direction flowing northwards into the Rockall Trough. The current at the surface was measured at an average velocity of 0.23 m/s^{-1} with velocities slowing down with depth to an average of 0.11 m/s^{-1} at the 1040 m.

Using literature data in addition to data from other Marine Institute surveys completed within the timeframe of the deployment and in the immediate vicinity of the weather buoy it was possible to compile a variety of physico-chemical data to support classification of the water masses in which PSDs were deployed. Salinity and

temperature values at the surface were measured at an average of 35.58 g/L and 10.96 ^{o}C respectively. These data support the findings of McGrath *et al.* [178] who reported temperature and salinity values for ENAW water at between 8 – 12 ^{o}C and 35.66 g/L respectively and which can be used to identify surface waters in the vicinity of M6 as ENAW. This water mass is formed in the Bay of Biscay before flowing northwards into the Rockall Trough.

Table 5.2: Summary physic-chemical via MiniCat (this study) and experimental parameters the M6 test site.

Parameter	0 to 5 m	225 to 275 m	650 to 725 m	957 to 1052 m
Water Mass*	**ENAW**	**ENAW/SAIW**	**ENAW/SAIW**	**SAIW**
Flow velocity	0.23	0.19	0.14	0.11
Measured R_s L/d (PDMS)	40	44.6	151	125
Silicate µmol/L*	3.16	3.16	8.57	10.52
Phosphate µmol/L*	0.57	0.53	1.07	1.13
TOxN µmol/L*	9.6	9.61	18.5	18.73
Salinity g/L	35.58	35.52	35.3	35.23
Temperature °C	10.96	11.17	8.85	6.58
Density	1027	1028	1030	1032
DO umol/kg	259	261	207	221
TA µmol/kg	2333	2333	2329	2321
DIC µmol/kg	2134	2129	2171	2174

* from McGrath *et al.* [178]

The Rockall Trough has been recognised as an important pathway for nutrient rich warm waters to enter Nordic seas.[182] As previously mentioned the upper 1000 m of water has been associated chemically with Eastern North Atlantic Water (ENAW) which is characterised by warm saline water and formed in the Bay of Biscay. The temperature range of this water is usually between 8 – 12 ^{0}C with salinity of ~35.66 g/L. [178] At the Southern entrance of the trough between 400 – 800 m salinity values fall indicating a mixing line between ENAW water and Sub-Arctic intermediate Water (SAIW). This highly stratified water mass is characterised by temperatures between 4 – 7 ^{o}C and a salinity of <34.9 g/L. SAIW is formed in the western boundary current of the

sub-polar gyre in the Labrador Sea.[179] At approximately 1000 m, Mediterranean Water (MW), can be found. This water mass, which is formed in the Mediterranean Sea, flows through the strait of Gibraltar where it spreads northward along the continental shelf and is characterised by a high saline content of ~ 36.5 g/L and a temperature of 11.5 ^{o}C It's properties are then diluted due to lateral mixing with the adjacent water masses present.[178]

Labrador Sea Water (LSW) is formed from deep water convection in the Labrador basin and is characterised by temperatures <2.82 ^{o}C and salinities <34.84 g/L. It can be identified between 1600 – 1900 m in the Rockall Trough.[179] Northeast Atlantic Deep Water (NEAD W) has a temperature range of 2.03 – 2.5 ^{o}C with salinity values between of 34.89 – 34.94 g/L and is found between 2000 – 3000 m. *Figure 5.4* (a) shows a cross section of salinity and depth in the Rockall Trough, indicating the different water masses present. The red line on the overlay map (b) outlines the transect positions where samples were taken.[178] Water masses outlined in the plot are; Eastern North Atlantic Water (ENAW); Shelf Edge Current (SEC); Mediterranean Water (MW); SAIW (Sub Arctic Intermediate Water); Labrador Sea Water (LSW) andNorth East Atlantic Deep Water (NEADW). The M6 weather buoy is located at 15.88 degrees west (Longitude) which puts it to the west of the Porcupine Bank above the deepest section of the Rockall Trough.

Overall miniCat CTD devices co-deployed with passive samplers during this study suggest that the upper and lower depth samplers (5 m – 1040 m) are primarily subjected to ENAW and SAIW current influences respectively.

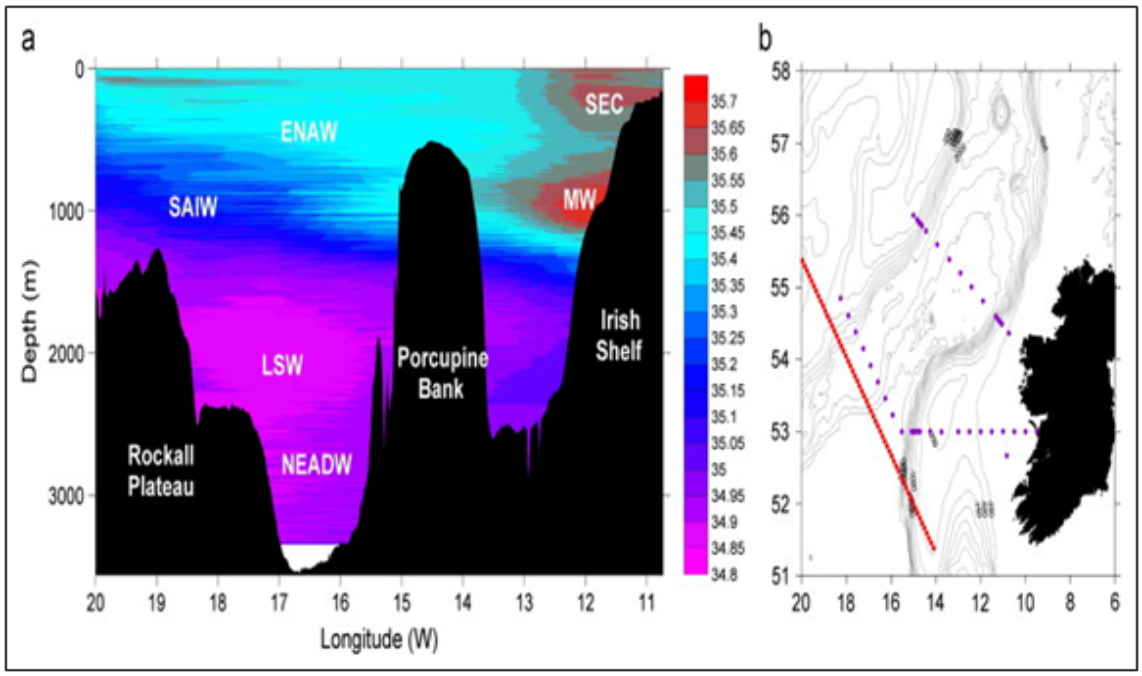


Figure 5.4 Cross section of salinity along a transect extending from the Irish shelf about 52 °N across the southern Rockall Trough reproduced from McGrath *et al.*[178]

5.2.2.2 Assessment of Performance of PDMS Passive Samplers

Sampler extracts were analysed by GC-MS and GC-ECD for PAHs and PCB/OC compounds respectively with the results shown in *Table 5.3* below. Further details on the methods used in the treatment of the data as presented in *Table 5.3* is shown in section 6.1.3.2.

Table 5.3 C_w concentrations (pg/L) for PAH, PCB and OCs at different depths for SPMDs and PDMS passive samplers deployed at the M6 weather buoy.

	250 m		750 m		1040 m		PDMS PSD			
Compound (pg/L)	**SPMD 1**	**SPMD 2**	**SPMD 1**	**SPMD 2**	**SPMD 1**	**SPMD 2**	**5 m**	**250 m**	**750 m**	**1040 m**
Acenaphthylene	32	41	35	24	29	33	36.8	5.56	4.22	2.89
Acenaphthene	22	23	17	15	15	12	42.0	7.54	4.20	3.54
Fluorene	61	65	53	51	44	43	50.0	20.4	11.2	10.9
Phenanthrene	176	184	174	162	133	143	406	308	328	210
Anthracene	11	12	12	11	10	11	10.2	16.5	19.2	10.9
Fluoranthene	23	23	92	87	66	83	38.9	37.5	95.6	78.9
Pyrene	5.7	5.3	15	14	12	15	14.0	6.16	10.8	8.68
Benz[a]anthracene	2.4	2.4	2.6	2.5	1.9	2.2	1.47	0.73	0.65	0.40
Chrysene	10	10	24	23	18	25	4.89	5.39	10.5	7.46
Benzo[b]fluoranthene	6.7	6.2	10	7.3	10	14	3.17	3.53	3.90	1.37
Benzo[k]fluoranthene	3.6	3.4	4.2	3.3	3.9	4.6	2.43	2.70	3.17	1.34
Benzo[a]pyrene	0.7	0.6	0.5	0.5	0.5	0.6	5.24	1.73	0.06	0.97
Indeno[1,2,3-cd]pyrene	0.3	0.1	0.3	0.1	0.4	0.8	0.64	0.15	0.02	0.08
Dibenzo[a,h]anthracene	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	0.08	n.d	n.d	n.d
Benzo(g,h,i)perylene	0	<0.01	0.3	0.2	<0.01	0.3	0.48	0.32	0.23	0.07
∑PAHs	354	375	438	401	342	388	617	416	492	338
Ratio P/A	16	15	15	15	14	13	39.8	18.6	17.1	19.2
Ratio FL/PY	4.0	4.3	6.2	6.1	5.6	5.4	2.78	6.08	8.85	9.10
LPAH/HPAH	5.7	6.4	2.0	1.9	2.1	1.7	7.64	6.16	4.28	2.40
PCB 18	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	0.4	0.3	0.9	0.5
PCB 28	1.0	0.9	0.5	0.6	0.7	0.6	0.4	0.3	0.6	0.4
PCB 31	0.7	0.6	1.2	1.8	0.7	1.0	0.4	0.4	0.6	0.3
PCB 44	1.0	1.0	1.6	1.6	0.9	0.8	0.2	0.3	0.9	0.4
PCB 52	1.0	0.9	1.2	1.6	0.3	0.2	0.1	0.3	0.9	0.3
PCB 101	0.3	0.3	0.5	0.4	0.4	0.4	0.2	0.4	0.4	0.3
PCB 149	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	0.1	0.2	0.3	0.1
PCB 118	0.6	0.6	1.5	1.7	0.6	0.5	0.2	0.2	0.2	0.3
PCB 153	0.9	0.9	1.9	2.0	1.8	1.9	0.2	0.4	0.3	0.3
PCB 105	0.3	0.3	0.7	0.8	0.1	0.1	0.3	0.8	0.8	0.3
PCB 138	0.4	0.4	1.1	1.2	0.7	0.6	0.6	0.4	0.3	0.1
PCB 156	0.1	0.1	0.2	0.6	0.1	0.0	0.0	0.1	0.3	0.1
PCB 170	0.1	0.1	0.3	0.4	0.3	0.3	0.1	0.1	0.1	0.1
PCB 180	0.1	0.1	0.1	0.2	0.1	0.1	0.03	0.1	0.010	0.02
PCB 194	K	K	K	K	K	K	K	0.13	0.02	0.02
PCB 209	K	K	K	K	K	K	0.003	0.24	0.15	0.1
α-HCH	32.9	34.7	46.1	56.6	36.1	34.7	143	104	89	72.5
β-HCH	n.d	n.d	n.d	n.d	n.d	n.d	267	265	173	149
Endosulphane sulphate	26.6	26.9	30.7	41.0	26.4	n.d	n.d*	n.d*	n.d*	n.d*
Lindane	34.8	35.3	22.8	11.5	31.5	71.4	n.d	n.d	n.d	n.d
op-DDD	0.05	0.06	0.80	0.74	0.43	0.37	n.d	n.d	n.d	n.d
op-DDT	1.31	1.86	3.70	4.98	3.52	4.25	<0.02	0.4	0.1	<0.02
pp-DDD	0.44	0.43	2.55	3.02	1.01	1.13	5	3.1	1.4	1.38
pp-DDE	0.98	1.10	4.36	4.96	2.72	4.15	0.1	0.2	0.3	0.15
pp-DDT	1.88	1.99	7.08	8.84	6.23	7.83	2	0.5	0.8	2.19
Trans chlordane	0.91	1.13	1.68	1.94	1.25	2.30	n.d	n.d	n.d	n.d
op-DDE	0.33	0.50	3.77	4.77	4.21	2.57	0.6	0.3	0.1	0.15
cis-chlordane	1.39	1.65	4.56	4.79	2.32	2.59	0.4	0.7	0.5	0.16
Dieldrin	4.96	4.65	33.7	78.1	52.3	28.7	2.1	1.4	2.3	1.13
HCB	12.1	12.3	16.2	19.0	13.0	15.2	0.1	0.3	0.3	0.86
Heptachlor	0.68	0.75	0.85	2.34	0.52	2.74	K	K	K	K
Oxychlordane	21.0	21.1	12.0	34.7	73.2	35.5	K	K	K	K
Heptachlor Epoxide	9.7	7.37	5.48	7.47	4.09	3.23	K	K	K	K
Trans-Nonachlor	0.75	0.80	0.49	0.55	7.11	7.39	K	K	K	K
Endosulfan	26.6	26.9	30.7	41.0	26.4	28.4	n.a*	n.a*	n.a*	n.a*
Endrin	10.3	11.1	15.9	16.5	9.6	12.5	K	K	K	K

n.d – not detected, n.a – not analysed, n.a* – interferent in chromatogram, K – concentration calculated no *Log* K_{pw} value

5.2.2.3. PAH C_w Estimation by PDMS

PAH concentrations (*Table 5.3*) were low overall with $\sum PAH_{15}$ ranging from 338 – 617 pg/L in the water column at 1040 and 5 m respectively. Phenanthrene was the major PAH found, contributing 62 – 74 % of the total $\sum PAH_{15}$ present in the samplers. Given the chemical nature of naphthalene, concentrations as derived via long term deployments are generally not reported and thus this was excluded. Naphthalene was additionally found at high levels in the blanks and T_0 (Appendix A.8 *Table 1*).

PAH concentrations in the surface sampler were higher (particularly lower molecular weight PAHs) than those at depth indicating that perhaps aerial deposition and/or surface deposition from passing marine traffic may be a possible source of PAHs in the surface sampler. It should be noted that only one PDMS sheet was recovered from the surface sampler therefore there is reduced confidence relative to data generated where multiple samplers were available. Low levels of higher molecular weight PAHs such as indeno(1,2,3-cd)pyrene and dibenzo(a,h)anthracene were found in all samplers apart from the surface (5 m) sampler, in some cases these compounds were not detected. These compounds, because of their chemical nature, may become absorbed to suspended particulate matter more easily than lower molecular weight PAHs,[183] hence it may be expected that the passive sampler available concentrations may decrease with depth.

5.2.2.4 PCB and OC C_w by PDMS

PCB results shown in *Table 5.3* are very low in comparison to results from inshore work reported in other sections in this study with the ∑PCBs ranging from 0.9 – 6.5 pg/L. Of the PCBs major contributions were noted from PCBs 31, 28, 55 and 105, 138 and 153. The levels of PCBs found are in agreement with those reported by Schulz-Bull *et al.* [184] where PCBs in the North Atlantic were measured between 0.347 – 11.24 pg/dm^3 and those reported in a Norwegian Institute for water research (NIVA) report [185] using PDMS and SPMD samplers where the levels of upper bound ∑PCB_{10} in PDMS PSDs were estimated at 29 pg/L.

Overall ∑PCBs increased slowly with depth up to and including 750 m samplers and then reduced at 1040 m. ∑OCs were found at highest levels in the surface sampler and were found to reduce with depth. Aerial deposition of OCs at the surface would appear to be the primary route of transport to this site. For OC compounds major contributions were noted from α and γ-HCH which are in agreement with the NIVA report [185] where these compounds were found in highest abundance in both SPMD and PDMS samplers deployed.

Levels of PCBs and OCs present in the PDMS samplers were found to be low overall with levels similar to those reported by Allan *et al.* [185] where HCHs were detected at low levels but higher than those of other OCs and PCBs. Overall OCs concentrations seem to be reduced at the lowest depth , this may be as expected given the remote area under investigation as OC compounds are generally deposited at the surface and the freely dissolved water concentrations would be reduced at depth through sorption with particulate matter.

5.3 Assessment of Performance of SPMD Passive Samplers

The extraction of SPMDs has been described extensively in the literature [94,186,187] hence will only be briefly described here. Each SPMD was individually removed from the storage container and immediately cleaned by scrubbing the SPMD surface and rinsing with de-ionized water, followed by a quick surface rinse with acetone then hexane. The cleaned SPMD was then placed in a contaminant-free glass container with an airtight lid containing a sufficient volume of hexane to cover the SPMD. The dialysis containers were then placed in an incubator at 18 ºC for 24 hours. After this first dialysis period, the hexane was transferred into a separate beaker and a second portion of hexane was added to the SPMD container. The second dialysis period was performed for a minimum of 6 hours at which time the hexane from both dialysis periods was combined and the SPMD discarded. The resulting combined hexane fractions were then dried down under a gentle nitrogen stream to ~ 2 mL.[187] To satisfy quality control aspects in relation to the extraction of SPMD sheets a quantification recovery standard (benzo(a)anthracene-$_{d12}$) was spiked onto two of the samplers at the beginning of the extraction.

5.3.1 Calculation of C_w for M6 SPMDs

SPMD passive sampler C_w concentrations were calculated in a similar manner to that of PDMS samplers (section 4.3.3). Briefly, the final extracts were firstly analysed for PRC compounds in the field control and the deployed samplers. Assessments were then made of the percentage PRC compounds remaining in the deployed sampler sheets. Extracts were then analysed for the compounds of interest with these final concentrations used to work out C_w concentrations for each of the samplers using an SPMD estimator as per Alvarez [133] which is a recognised method as used by the United

States Geological Survey (USGS) for the purposes of estimating SPMD modelled data. Results (ng/sampler) are shown in Appendix A.8 *Tables 1,2* and *3.*

5.3.2 Generation of C_w using SPMD Calculator

In the case where PRC data is not available (*e.g.* fully dissipated or where PRCs have not been used in the SPMD set up), then a site specific sampling rate (R_s) cannot be calculated. To finalise a C_w value, experimentally derived compound specific sampling rates (K_{SPMD}) were used (where available) for the compounds of interest. This method uses mathematical models where the various regimes of passive sampling (kinetic or equilibrium, chapter 2) are described using separate equations.

Firstly a compound specific theoretical half life ($t_{1/2}$), of a PRC in a sampler is calculated based on the length of deployment time and the K_{SPMD} value for each compound.[133] Using the appropriate mathematical model concentrations (ng sampler) found in the analysed SPMD can be converted into an estimated dissolved concentration and be reported on a pg/L basis. The dissolved water concentrations were calculated using the Excel spreadsheet created by Alvarez [187] which takes into consideration a number of variables including the individual sampler specifications (length, weight of triolein, average mass of sampler) as well as the deployment duration and average temperature of the water present at the sampling site. Log K_{ow} values are used to calculate a compound specific K_{SPMD} which can then be used to calculate a laboratory derived sampling rate (R_s) for a given compound (L/d) which was used for measurement of final C_w values for each compound.

5.3.3 PAH C_w by SPMD

PAH data on a ng/sampler basis (appendix A.8 *Table 1*), were used in conjunction with the SPMD C_w calculator to derive C_w values for PAHs (see *Table 5.3*) in pg/L. Naphthalene concentrations are again not reported as a high LOD was measured in all SPMD extracts, including blanks. $\sum PAH_{15}$ results were all similar in concentration ranging from 342-438 pg/L and are all low in comparison to PAH values from coastal sites around mainland Ireland (ng/L basis) discussed in chapter 6 of this thesis.

Major contributions to the $\sum PAH_{15}$ are noted from phenanthrene, fluoranthene and fluorene with average percentage contribution values of 42.5, 16 and 13.8 % respectively. Derived concentrations compare well to Lohmann *et al.* [188] where phenanthrene, fluoranthene and pyrene were major contributing PAHs detected with average values of 170, 30 and 70 pg/L. These data were taken from measurements of direct sea water and polyethylene passive samplers from Atlantic surface waters. Schulz-Bull *et al.* [184] report levels of $\sum PAH_6$ ranging from 5 – 65 pg/dm^{-3} in water samples from the North Atlantic ocean near Iceland. Again the major contributors to the $\sum PAH_6$ measured by Schulz-Bull *et al.* [184] were phenanthrene, fluoranthene and pyrene.

NIVA[185] report both PDMS and SPMD sampling devices along the Norway coast with levels of $\sum PAH_{18}$ at 1.82 ng/L for PDMS and 0.74 mg/L for SPMDs recorded. Booij *et al.* [189] report that PAHs in SPMDs deployed in air and water along a transect from Texel (Netherlands) to Capetown, South Africa were found at low levels (< ng/L) with major contributions from phenanthrene, fluoranthene and pyrene.

Despite the length of deployment at the M6 weather buoy only trace amounts of the heavier (6 ring) PAH compounds were found with concentrations generally at or below the limit of detection.

5.3.4 PCB C_w by SPMD

PCBs in SPMDs (pg/L) were low overall ranging from 0.06 – 2 pg/L with the $\sum PCB_{12}$ measured ranging from 6.26 to 12.7 pg/L. Major percentage contributors to the $\sum PCB_{12}$ were from congener 153, 52 and 28 (average of 20, 14.1 and 12 % respectively). The $\sum PCB_{12}$ levels were lower at 250 and 1040 m than at 750 m. NIVA[185] report upperbound levels of $\sum PCB_{10}$ at 0.029 ng/L for PDMS and 0.034 ng/L for SPMDs which are within in the concentration ranges for PCBs reported in this study (*Table 5.3).*

Evaluation of the $\sum PCB_7$ common "indicator" congeners ranged from 4.04 - 9.09 pg/L in comparison to 0.019 – 0.026 ng/L for the NIVA Norwegian samplers.[185] Schulz-Bull *et al.* [184] report PCBs in the range <2 – 126 fg dm^{-3} in solution and 286 – 1400 fg dm^{-3} in suspension with particulate matter using water samples from the North Atlantic area. The Schulz-Bull *et al.* [184] study indicates that surface water samples at different sites (n =4) exhibit the highest levels of PCBs ($\sum PCB_{23}$ ranging from 0.347 - 11.24 pg/dm^3).

5.3.5 OC C_w by SPMD

OC C_w were low overall with hexachlorohexane (α and γ) compounds exhibiting the highest levels of the OCs found. Again OC concentrations appear, in general, to be more elevated at the 750 and 1040 m SPMDs when compared to the values calculated

for 250m SPMD. The NIVA study [185] reports that levels from the Nordic seas in relation to six OCs calculated ranged from 0.0025 – 1.1 ng/L with α and γ-HCH (lindane) dominating the overall percentage contribution, the sum of the same 6 OCs in this present study was measured at 77.2 - 150 pg/L at the M6 location. Booij *et al.* [189] report that the levels of pp-DDE and HCB in the North Atlantic range between 1.9 – 9.0 and 0.3 – 1.4 pg/L respectively which are in close agreement with values reported here (*Table 5.3*).

5.3.6 Quality Control of SPMD Concentrations at M6

To satisfy quality control issues in relation to analysis of SPMD passive samplers at the M6 site, a number of steps were taken including the use of spikes, procedural blanks and replicate analysis of samplers. A recovery standard (benzo(a)anthracene-$_{d12}$) was spiked onto two of the samplers at the beginning of the extraction with recoveries of 97.6 and 84 % calculated thus extraction was deemed exhaustive. Replicate SPMD samplers were present at each depth and a students t test performed on the duplicate SPMD data ($\alpha = 0.05$, critical value = 2.04) for all compounds from each depth. The results of this analysis $t(6) = 2.04$, $p < 0.05$ were 0.09, 0.7 and 0.25 for 250, 750 and 1040 m SPMDs respectively indicating that the contaminant data did not differ significantly between replicates.

5.3.7 Discussion of the M6 SPMD Results

In the absence of full PRC data from the SPMD passive samplers at the M6 site the method of Alvarez [133] was used for the generation of C_w concentrations. Overall the concentrations of all contaminants found were low and comparable to relevant open

water literature which is to be expected given the remoteness of the location. The power of passive sampling as a technique to accumulate contaminants at extremely low levels (<ppb) was illustrated. Overall SPMDs fared better in a physical sense in this environment than did the PDMS samplers deployed with a lower attrition rate observed for SPMDs.

PAH concentrations in SPMDs (*Table 5.3*) were low (<ppb) in all of the samplers with the $\sum PAH_{15}$ highest in the 750 m sampler. PAH profiling suggests that the PAHs at this site in all depths are mixed and/or petrogenic in nature. This is to be expected in a remote site where pyrogenic sources may not be present. PAH profiling (*Fig 5.5)* suggests petrogenic influences as the ∑LPAHs/HPAHs ratio is greater than 1 for all depths.

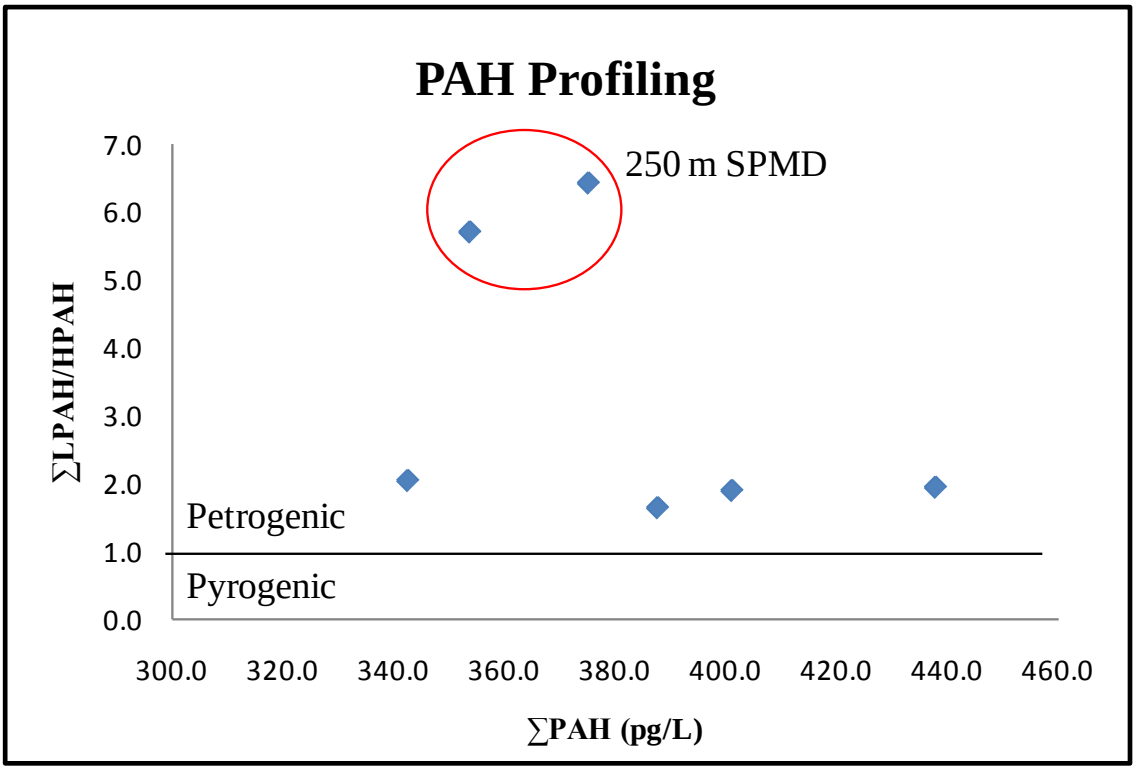


Figure 5.5 PAH profiling of SPMD PAH concentrations using ∑LPAHs/HPAHs vs ∑PAHs.

The ratio of ∑LPAHs/HPAHs in the 250 m sampler were found to be higher than those in deeper water, 5.7 and 6.4 in 250 m SPMDs compared to an average of 2.0 for the deeper SPMD samplers *(Fig 5.5)*. Phenanthrene levels were found to remain consistent across all depths but the levels of fluoranthene, pyrene and benzo(a)anthracene doubled (approximately) in the 750 and 1040 m samplers. All other contaminant levels remain relatively similar throughout the samplers at all depths. This may indicate a change in PAH loadings at 750 – 1040 m which may be a reflection of the influence of different water masses at these depths.

SPMD concentrations (pg/L) for PCBs at the M6 weather buoy are very low overall (*Table 5.3*) with the $\sum PCB_7$ ranging from 4.04 – 9.09 pg/L. In this case the profile suggests that PCBs from 250 m and 1040 m are very similar but that the PCBs at 750 m are elevated in comparison, see PCA plots (*Fig 5.6 – 5.8*) for further evaluation of contaminant profiles.

5.4 Comparison of SPMD and PDMS Data

This study used two of the more popular types of passive sampler to estimate the levels of organic contaminants present in the waters at M6. The SPMD is a bi-phasic sampler with triolein as a receiving phase where as the PDMS is a single phase type of sampler. Both types of sampler work in a similar manner sequestering contaminants from the surrounding medium but the modelling of contaminant uptake in the SPMD, because of the different phases involved, is more complex than the single phase PDMS sampler.

While the extended deployment period is not optimal for the performance of both sampler type analytical data both initial sampler concentration data and final modelled data can be further evaluated to compare sampler performance relative to each other. This was completed in a number of stages as follows;

a) General discussion of modelled parameter data,
b) Statistical comparison of modelled data for both SPMD and PDMS,
c) Assessment of parameter uptake ratios to evaluate uptake versus modelling effects.

5.4.1 General Discussion of Modelled Parameter Data

Overall the general performance of both samplers was similar with concentrations of PAHs between the two samplers at M6 broadly very similar. Benzo(a,h)anthracene was detected at below the LOD (0.08 pg/L) by both devices while phenanthrene had the highest levels of any of the PAHs detected in either sampler ranging from 133 – 406 pg/L for the 1040 m SPMD and 5 m PDMS respectively.

The C_w concentrations of phenanthrene (pg/L) in the PDMS samplers appear elevated in comparison to the levels found in the SPMDs. When comparing the percentage contribution of phenanthrene to the $\sum PAH_{15}$ this difference is again highlighted. In the SPMDs, phenanthrene contributes 37 – 50 % of the total $\sum PAH_{15}$ present where as in the PDMS the contribution from phenanthrene makes up 50 – 74 % of the $\sum PAH_{15}$. The percentage contribution of phenanthrene to the $\sum PAH_{15}$ at the M6 site in SPMDs are similar to values reported by Karacik *et al.* [190] while $\sum PAH_{16}$ using SPMD in the black sea showed that phenanthrene contributed 16 – 50 % of the total PAH present. Monteyne *et al.* [173] show that the percentage contribution of phenanthrene to the total

PAHs present in PDMS passive samplers at three Belgian coastal harbours ranged from 1.7 – 48 %.

PAHs accumulated in the PDMS PSDs appear to be in highest concentration at the surface dropping off slightly at depth (with exception of 750 m). A similar profile is detected in the SPMDs where the 750 m $\sum PAH_{15}$ concentrations appear elevated compared to the other depths.

Concentrations (pg/L) estimated for PCB/OCs in both SPMDs and PDMS samplers at the M6 site are at very low levels and once again at a similar concentration. For OC compounds the highest levels found in both sampler types were the HCH compounds (α and γ HCH). Fewer C_w data are available for OC compounds in PDMS passive samplers in comparison to SPMDs because, as of the time of analysis fewer *Log* K_{pw} values calculated using the co-solvent method are available for PDMS OC compounds. For SPMDs no final C_w values are present for PCBs 194 and 209 as the SPMD calculator does not estimate these values because they are not accumulated to any great degree.

5.4.2 Statistical Evaluation of PDMS vs SPMD Performance

In order to further evaluate sampler performance and to further investigate the potential effect/performance of each sampler type at depth, final modelled analytical data were normalised relative to the modelled concentrations determined in the SPMD sampler at 250 m (replicate 1). This process of normalising sampler performance relative to one single device enabled concentration independent profiles be assessed and compared for all samplers (*Table 5.4*).

Table 5.4: Correlation (Pearson R) of normalised PAHs concentrations between SPMD and PDMS at depths where both samplers were available.

Depth	250 m	750 m	1040 m
250 m	0.948	NA	NA
750 m	NA	0.939	NA
1040 m	NA	NA	0.947

Normalised modelled PAH concentrations were evaluated in order to determine the level of correlation between devices at 3 sampling depths. Strong correlation (R = 0.939 to 0.948) was shown to exist between the final concentrations measured by both sampler types irrespective of depth sampled. This demonstrates that both samplers behaved similarly at each of the 3 depths.

Similarly evaluation of the performance of each device type was completed relative to sampling depth. It is clear that normalised PAH profiles in both PDMS and SPMD devices show strong correlation irrespective of the depth sampled (*Table 5.5*).

Table 5.5: Correlations (Pearson R) of PAH concentrations in SPMD and PDMS at 3 depths. PAH concentrations relative to SPMD replicate 1 at 250 m.

	PDMS				SPMD		
	5 m	250 m	750 m	1040 m	250 m	750 m	1040 m
5 m		0.992	0.966	0.948	None	None	None
250 m	0.992		0.984	0.968		0.917	0.917
750 m	0.966	0.984		0.997	0.917		0.999
1040 m	0.948	0.968	0.997		0.917	0.999	

The overall collective performance of SPMDs and PDMS for the analysis of the full suite of PAHs has been demonstrated to be similar irrespective of depth. This assessment does not however evaluate whether concentrations of the different PAH

change with depth itself. Lower correlation was calculated for between PDMS and SPMD (R = 0.42 to 0.52) for PCBs.

Table 5.6 details normalised SPMD and PDMS PAH concentrations relative to SPMD replicate 1 at 250 m. Potential correlation between the relative percentage of each PAH present and the depth of deployment was evaluated by generation of Pearson correlation coefficients (R) between the relative percentage of each PAH present and its associated sampling depth. It is clear relative concentrations of acenaphthene, fluorene, chrysene and phenanthrene decrease with depth while fluoranthene, pyrene and benz[a]anthracene increase with depth. This is not unexpected given the Log K_{ow} of compounds and their relative capacity for absorption to particulate as previously discussed.

Table 5.6: SPMD and PDMS PAH concentrations as a percentage of concentrations determined in SPMD replicate 1 at 250 m. Pearson coefficient R denotes correlation and direction or relationship between individual PAH and associated sampling depth for both SPMD and PDMS respectively.

		SPMD								PDMS					
Compound	**LogK_{ow}**	**250(1)**	**250(2)**	**750(1)**	**750(2)**	**1040(1)**	**1040(2)**	**Direction***	**Pearson**	**5**	**250**	**750**	**1040**	**Direction***	**Pearson**
Acenaphthylene	3.26	100	120	87.9	66	93.1	94.3	Weak Down	-0.527	66.1	14.8	9.5	9.5	Down	-0.775
Acenaphthene	3.62	100	99.6	62.5	59.7	69.4	49.5	Down	-0.901	111	29.7	14	17.2	Down	-0.797
Fluorene	3.79	100	100	69.9	74.6	75.3	64.2	Down	-0.927	47.3	28.6	13.3	18.8	Down	-0.869
Phenanthrene	4.11	100	98.7	79.9	81.3	78.2	74.3	Down	-0.974	132	148	134	125	Weak Down	-0.556
Anthracene	4.21	100	106	85.3	87.5	90.3	89.8	Down	-0.808	53.3	127	125	103	Weak up	0.506
Fluoranthene	4.62	100	94	325	337	299	334.1	Up	0.905	98	139	301	362	Up	0.995
Pyrene	4.68	100	87.8	211	221	214	247.1	Up	0.948	141	91.9	136	159	Weak up	0.533
Benz[a]anthracene	5.32	100	88.9	186	194	180	220.2	Up	0.93	27.3	44.5	73.4	76	Up	0.975
Chrysene	5.25	100	93.2	85.9	92.4	82.8	85.4	Down	-0.877	35	25.8	19.4	17.4	Down	-0.951
Benzo[b]fluoranthene	5.74	100	87.3	121	96.6	148	191.3	Up	0.808	27.4	45.1	42.2	21.6	None	-0.259
Benzo[k]fluoranthene	5.74	100	89.4	94.2	82.2	113	118.5	Weak up	0.573	39	64.1	63.7	39.3	None	-0.026
Benzo[a]pyrene	5.69	100	81.5	66.2	72.3	75.2	77.6	Weak Down	-0.643	456	222	6.5	154	Down	-0.781
Indeno[1,2,3-cd]pyrene	6.06	100	45.4	86.9	32.7	164	281.1	Weak up	0.644	136	47.2	5.3	31.1	Down	-0.794
Benzo[g,h,I]perylene	6.02	100	3.5	83.9	52.3	3.8	88.1	None	-0.025	102	100	61.3	27.2	Down	-0.971

*Correlations: None R<+/-0.50, weak R+/-0.5 to 0.75, strong R>+/-0.75. $p = 0.05$

5.4.3 Principal Component Analysis: PAH

In the case of PAHs, on a concentration basis it is clear that phenanthrene is a dominant analyte present with this being especially true for the PDMS samplers at upper depths relative to the SPMD devices. It is also clear that fluoranthene concentrations are a key driver in respect of deeper waters.

The PC1 annotation in *Fig 5.6* shows a geographical separation between PDMS and SPMD samplers while PC2 shows SPMD samplers at 250 m are seen to be geographically separated from those at 750 and 1040 m indicative of differences in concentrations and/or profile at 250 m relative to those at in deeper waters (see *Fig 5.6*). Concentration independent PCA plots (see *Fig 5.7*) normalised relative to fluoranthene, as this is seen to change at depth, further confirm separation of these 250 m samplers from SPMDs in deeper waters again further confirming that both the concentrations of PAHs and the observed profile differ in 250 m SPMD samplers relative to those from deeper waters. As per the concentration plots good replication in PAH profile was evident between replicates.

While the PDMS PAH profiles are geographically separated from those of the SPMDs (*Fig* 5.7) again it is clear that the PDMS profiles in deeper waters better resemble each other compared to samplers used in the surface water. The profiles of these deeper water PDMS devices are closer in agreement with the SPMD devices from similar depths.

Overall good replication was evident for the individual replicate SPMDs with replicate samplers at the 250 1040 and 750 m depths mirroring each other. PDMS profiles differ from those in SPMDs but overall good agreement is evident especially for samplers in deeper waters. With this general level of agreement between replicates of devices and between PDMS and SPMDs in deeper waters it is suggested that differences in PAH profiles may be more pronounced in upper waters (dominated by lower Log K_{ow} parameters).

5.4.4 Principal Component Analysis: PCBs

As expected PCB 153 in the dominant congener in all samplers. Concentration independent PCA profiling (*Fig 5.8 and 5.9*) further suggests strong PCB profile similarities between replicate SPMD samplers and between sampling depths suggesting that the PCB profile remains relatively unaltered through the water column. While good similarity between replicates is also observed in concentration based PCA plots replicates at depth are more spatially disparate. This suggests that while the PCB profile remains similar throughout the water column that PCB concentrations differ.

PDMS samplers behaved somewhat differently with a wider spatial spread in respect of PCB profiles. More elevated PCB 52 and PCB 44 concentrations dominate the profile of the 750 m PDMS sampler while PCB 138 is a key contributor to the 5m PDMS sampler (no SPMD sampler was available at this depth). With the exception of the 750 m PDMS sampler, PDMS and SPMD concentration independent profiles were spatially similar for both PDMS and SPMD. Concentrations of PCBs in PDMS

were found to be relatively similar through the water column. Overall it can be concluded that SPMDs performed relatively similarly in respect of replicates (further validating the spiking process) and that the profile of PCBs is shown to be more conservative (relative to differences observed for high and low molecular weight PAHs) through the water column.

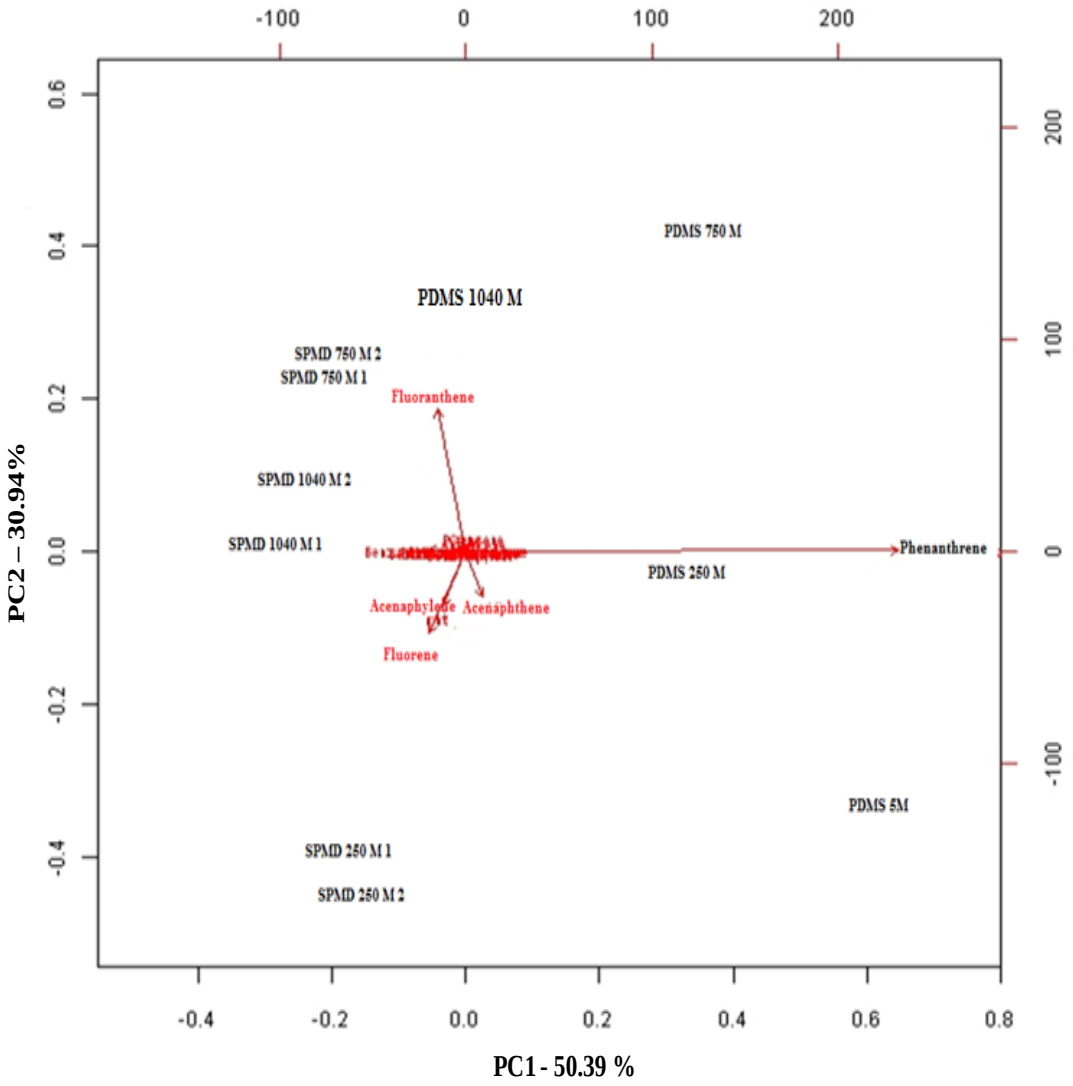


Figure 5.6: PCA bi-plot of PAH concentrations in PSDs.

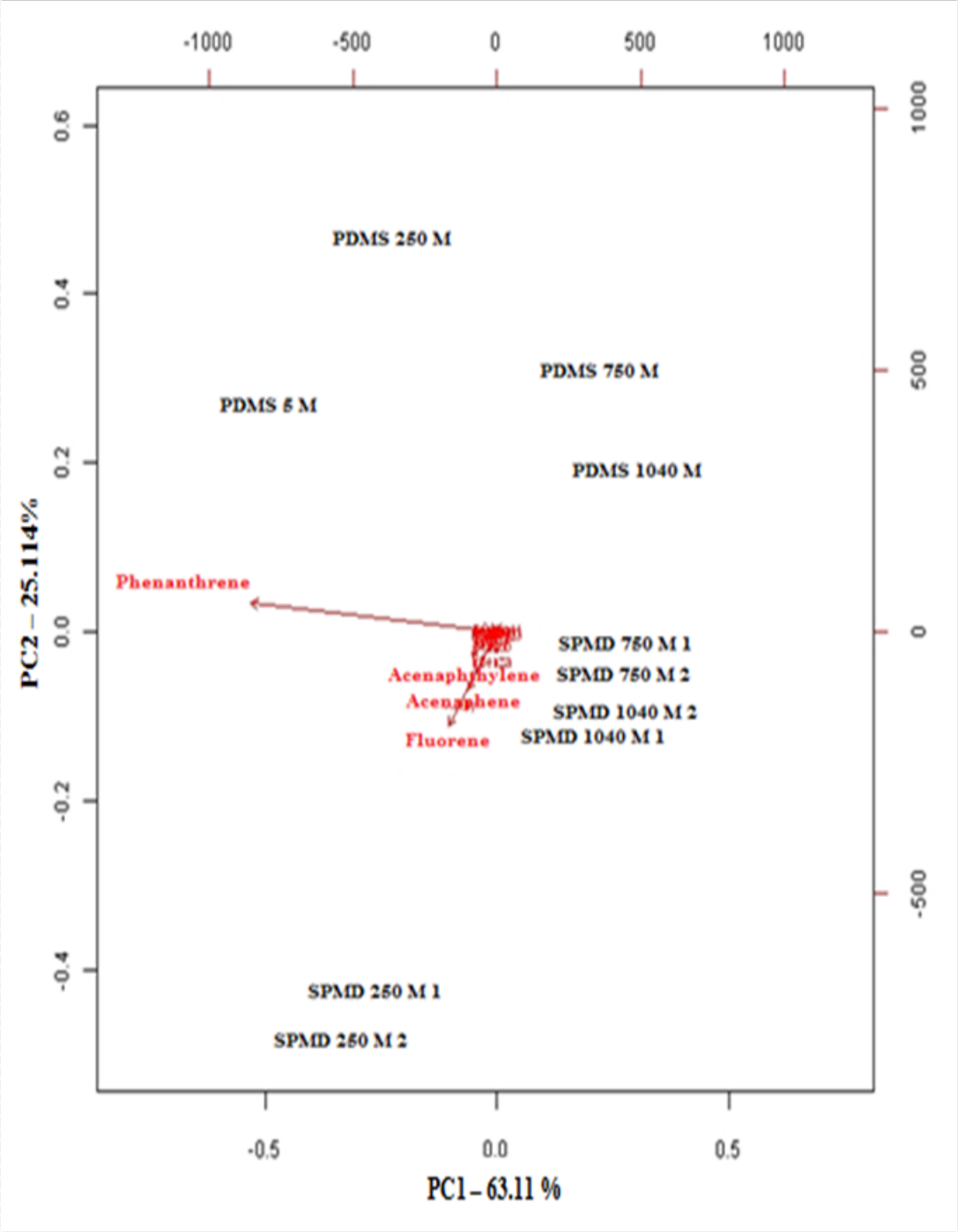


Figure 5.7: PCA Bi-plot of PAH in PSDs relative to concentration of fluoranthene

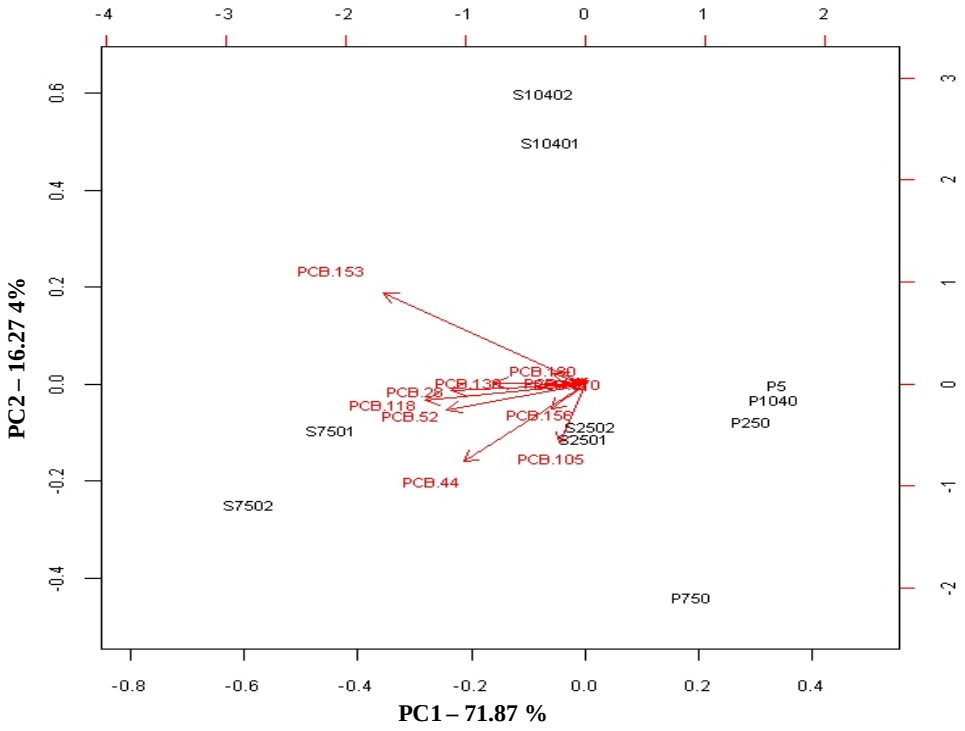


Figure 5.8: PCA loading plot of PCB concentrations in PSDs.

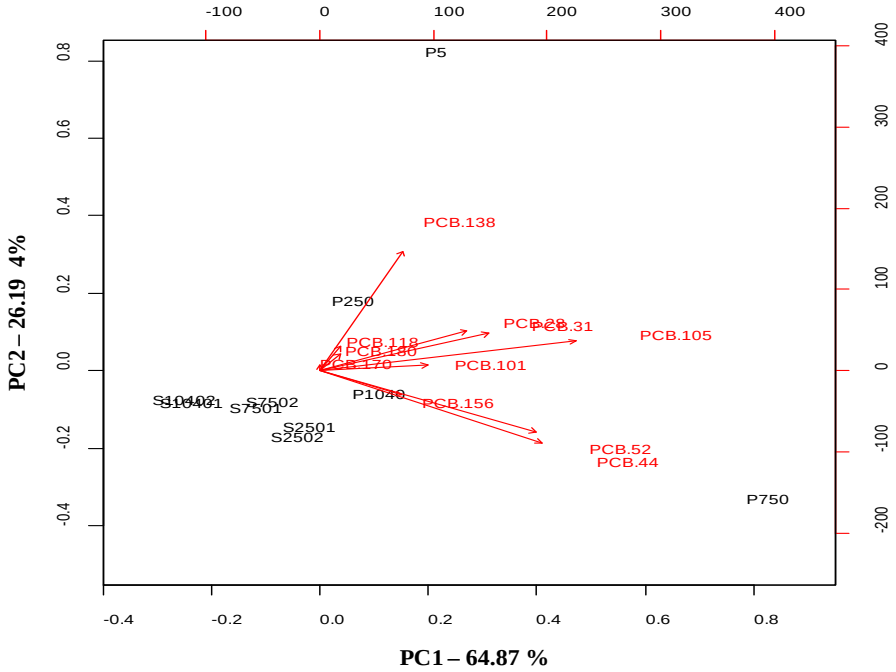


Figure 5.9: PCA loading plot of PCBs in PSDs relative to concentration of PCB 153

5.5 Overall Conclusions and Recommendations

This study has provided valuable concentration and profile data for a variety of persistent pollutants, few such data are available in the literature. Such “baseline” dissolved water concentration data from “pristine” offshore waters are of great value in ongoing discussions regarding the relevance and applicability (and in the generation of legislative thresholds) of passive sampling in a wider monitoring context. Overall concentrations of PAH, PCBs and OC were low and comparable with the few studies available from open waters.

Increases in the concentrations of fluoranthene, pyrene and benzo(a)anthracene congeners, and decrease of acenaphthalene, fluorene and chrysene at depth indicate that the contaminant profile changes relative to sampling depth possibly due to a change in contaminant profile.

Individual sampler types were shown to behave relatively similarly irrespective of depth but in the absence of sufficient replicates further research is merited to evaluate whether the major contributor to profile changes is related to different pollutant burdens associated with the relevant water mass or whether physico-chemical/adsorptive properties of the individual PAHs is the main driver of the observed profiles.

It is suggested that the uptake of some lower Log K_{ow} compounds reached equilibrium prior to the deployment finishing. This finding is of importance as such information are required in order to ensure that concentration data be calculated using appropriate procedures and that inappropriate data are omitted from processes

for the generation of future assessment criteria. The application of PCA profiling further supported sound application of initial spiking processes in addition to showing the relative robustness of sampler replicates.

It will not always be possible to deploy and retrieve PSDs within closely stipulated timeframes especially in offshore often dynamic locations. It is clear however that while controlled deployment times are advisable it is still possible to derive valuable monitoring information with PSDs deployed over an extended period. The application of contaminant profiling and/or normalisation techniques has proved to be a valuable tool in data interpretation.

It is further advised that great care in interpretation of modelled data whether it is from saline or freshwater environments is required to ensure that monitoring data are fit for purpose. It is further advised that such information be compiled to ensure data selected for the purposes of WFD background assessment criteria (BAC) generation are appropriate.

Few legislative thresholds currently exist in respect of PSD derived concentration data however it is only through such studies that “validation” of the technique can be further completed to progress the development of PSD derived monitoring and assessment criteria. As legislative limits continue to require lower limits of detection it is evident that “new” means of quantification such as the potential offered by PSD techniques is becoming more relevant. It is ultimately clear that there is an ongoing role for the continued development of these tools in the provision of a means by which sound environmental assessments may be completed.

Chapter 6: PDMS Passive Sampling of Hydrophobic Pollutants in Irish Waters

6.1 Introduction

One of the key objectives of this applied thesis is the evaluation of the applicability of using PDMS passive sampling derived time weighted dissolved water concentrations of contaminants in the support of routine environmental monitoring programmes. PSDs were deployed to sample a variety of locations and hydrodynamic conditions for a range of environmentally relevant contaminants with the ultimate aim of evaluating applicability of PSDs to satisfy various monitoring and legislative requirements. This chapter discusses key technical guidance in respect of the generation of quality assured PSD data and presents key datasets and discusses pressures and impacts at the sites tested.

Case studies as presented in chapters 4 and 5 have described the preparation, spiking and deployment of PSDs in freshwater and offshore locations. This current chapter further evaluates data obtained from a wide variety of other sampling sites and elucidates the extent of pollutant loadings at these locations. This chapter also discusses the applicability and potential implications/downsides as well as the crucial technical aspects that need to be adhered to in order for passive sampling based techniques to be considered as an effective monitoring tool capable of routine use which can then satisfy a variety of legislative requirements. Technical aspects include the evaluation of the effect of salt water on the performance of passive samplers and the effects on final C_w concentrations in both marine and transitional (mixed salinity) waters.

It is unclear whether “salting out effects” have been evaluated when preparing current assessment criteria, thus this chapter further evaluates the potential effects of

this phenomenon on derived water concentrations. It is further envisaged that over time such criteria can evolve in order to form a more relevant data set by which all other passive sampling data can be compared, given the relative paucity of such spatial passive sampling data the information provided within this thesis is of great value.

6.1.1 Experimental Design

The chapter aims to build on the case studies discussed in chapters 4 and 5 and to further ascertain the usefulness of PSDs as a tool to assess the dissolved water concentrations of contaminants of interest across a variety of sites and hydrodynamic conditions and to discuss whether concentrations estimated by the devices can be used to satisfy legislative requirements including the WFD.

To this end, two large-scale deployments of passive sampling devices took place during this stage of the project;

1) An initial deployment (at a number of project/non-WFD sites) took place in the summer/autumn of 2011,
2) A second deployment (at newly designated WFD sites) took place in the autumn of 2012. Passive sampling was selected as a means to determine water quality at these WFD sites only where no biota, routinely used in MI monitoring programmes (predominantly *Mytilus edulis*), was available but where water quality sampling was mandated.

For the first deployment (Project/non-WFD), a number of relatively industrialised, larger population centre sites (possibly with higher contaminant levels) in Ireland were chosen, including Dublin and Cork. Other sites selected included those exhibiting a variety of pressures and impacts ranging from Wexford harbour, Shannon harbour, Bantry bay and at the waste water treatment outflow at Mutton Island (Galway). Samplers were also deployed at a reference/control site (Omey Island, Co. Galway) to estimate what the response would be for a device deployed in a sparsely populated area with little in the way of anthropogenic pressures.

The second deployment took place in the autumn of 2012 as part of official WFD monitoring in locations for which no biota was available during sampling. The absence of biota at these sites is primarily as a consequence of the water body type with the selected sites being either estuarine or riverine in nature. A marine reference site in Kilkieran bay on the Irish west coast was also selected as being representative of low level marine pressures. Monitoring, using PSDs, included 15 WFD sampling sites from all across Ireland including the North Western Atlantic seaboard (NWA) and a number of inshore estuaries in the south of Ireland including the Nore and Suir (further details of locations are shown in *Table 6.3*).

The ultimate purpose of these deployments (and this chapter) is to further document the application of passive sampling for compliance monitoring, to compare contaminant profiles at sites with differing pressures and to generate assessment pilot criteria relevant in an Irish context (Irish Reference concentrations - IRef). Data are then further evaluated in respect of available assessment criteria, including the WFD in chapter 7.

Overall the key aims of this section were;

1. Generation of C_w data for PAH, PCBs, OC and PBDEs from a variety of locations, hydrodynamic regimes and pressures/impacts around Ireland;
2. Commentary on the use of QA in support of derived concentrations;
3. Evaluation of the salting out effect on passive sampler data;
4. Completion of site by site and parameter group profiling of generated PSD data;
5. Comparison of derived data to other PS literature data.

6.1.2 Generation of Passive Sampler Data

Passive samplers were fabricated and spiked in the manner set out in appendix A.6. They were frozen and placed in a cool box for transportation to the deployment sites where, along with a suitable field control they were deployed and retrieved (as per appendix A.6.) once the deployment period had ended and placed in a freezer (-28^{o}C) prior to analysis.

A total of 24 deployments of passive samplers took place over the course of this phase of the study. Of those 24 deployments only two sampler cages were lost, one at Sheep head in Bantry bay and the other at the Barrow Nore estuary, in both instances the whole mooring buoy to which the sampler cages were attached were lost. During all deployments no individual PDMS sheets were lost indicating that the current PSD set up including cage and supports for membranes is robust and ideal for sampling inshore and inland sites including rivers, lakes and estuaries for a period of 2 – 4 months, a timeframe currently deemed suitable to allow the sampler accumulate contaminants.

The extraction and analysis of all passive samplers took place in the manner outlined in section 3.5.1 where passive samplers were Soxhlet extracted using acetonitrile:methanol (3:1 v/v) before being cleaned up using silica gel, with the extracts being concentrated in 2,2,4-trimethylpentane before analysis was complete using GC-MS and GC-ECD following the techniques described in chapter 3.

6.1.3 Calculation of C_w Concentration for Passive Samplers.

As previously stated the calculation of C_w concentrations for PSDs deployed in this study was calculated in a stepwise manner:

1. Calculation of responses for PRCs found in field control, preparation controls and in exposed samplers, and the calculation of *in-situ* sampling rates (R_s),
2. Addition of external standards and calculation of concentrations (ng/g) in the PSDs, including quality control information,
3. Calculation of C_w concentrations from PSDs.

In addition to the steps outlined above an additional step was required in the analysis of R_s and C_w values as in this case the samplers were not only deployed in fresh water but in a mixture of marine and fresh waters. To this end the Setschenow [114] constants were again applied (as per chapter 5) initially in the calculation of *Log* K_{pw}^{so} values and subsequently in the calculation of R_s and C_w where applicable, as per Smedes and Booij.[115]

6.1.3.1 Calculation of in-situ Sampling Rates (R_s)

In previous chapters (4: freshwater and 5: oceanic) the calculation of the *in situ* R_s involved a calculation of the degree of similarity between measured dissipation curve PRC responses from deployed samplers (N_t) and those used as preparation controls (N_0). All PRC results and calculated R_s values are presented in appendix A.9 *Table 1*. The R_s was calculated in a stepwise manner as detailed below:

- Calculation *Log* K_{pw} and *Log* K_{pw}^{so} values for all compounds in the study;
- Calculation of PRC responses from extracted sampler sheets;
- Calculation of the *in situ* sampling rate R_s using Excel programme.

In this current deployment the sampling locations were of mixed nature with ~60 % being marine sites. Jonker and Muijs [113] discuss the aqueous solubility of organic chemicals in the marine environment noting that the increasing hydrophobicity of these chemicals in salt water as opposed to fresh water must be taken into account to avoid erroneous results. Smedes and Booij [115] also discuss the effects of salt water on the estimated *Log* K_{pw} values for PDMS passive samplers.

Since the upload and offload kinetics of passive samplers are assumed to be proportional [13, 85, 91] the salting out effect can be assumed to have a similar affect on the PRCs spiked into the sheets before deployment. The use of PSDs in such a range of sampling sites (fresh and marine waters) presents an opportunity to study the effect of using *Log* K_{pw}^{so} values on the calculation of R_s and subsequently C_w in marine sites in comparison to fresh water sites. The modelling and the subsequent affect on the final R_s and C_w values are further investigated in section 6.1.4.

6.1.3.2 Calculation of Passive Sampler and C_w Contaminant Concentrations

The calculation of passive sampler contaminant concentrations is discussed in section 4.4.2.3 and so will not be further discussed here. All results (ng/sampler basis) are shown in appendix A.9 *Table 1*. The C_w concentrations of all contaminants are broken down into sections depending on contaminant type and location and are

reported below (*Table 6.3*). The NLS method in conjunction with co-solvent derived *Log* K_{pw} values and estimated *Log* K_{pw}^{so} values [115] were used to calculate R_s and finally C_w concentrations as reported in *Table 6.3*. PAHs and OCs are reported on a ng/L basis with PCBs and BFRs shown in pg/L.

For the purposes of data assessment analytical data were treated as follows;

1) Where a "less than" (<value) is reported, the concentration of the analyte in question found, on a ng/sampler basis was greater than the limit of detection of the technique calculated from using the Field control or T_0 (shown in section 3.5.2.3.) This value was then used to derive "less than" C_w values as shown in *Table 6.3*. As this thesis generally adopted a precautionary approach only in terms of assessment, upperbound data were used in statistical assessment where the LOD was deemed to be sufficiently low to ensure that undue analytical based bias was not introduced into the overall statistics.
2) In cases where an n.d. (not detected) is reported, this represents the fact that no discernible chromatographic peak has been detected.
3) An n.a value is used where the compound was not analysed (BFRs primarily).
4) An n.a* is indicative of analytical interference in the chromatogram having been encountered making correct quantification of the analyte impossible. This information is reported to ensure that such interferences be further addressed during future analysis. No data where n.a* is present, were utilised in statistical aspects of the thesis to ensure no detection limit bias was inadvertently applied to the analysis.

5) A K value represents the fact that a concentration on a per sampler basis was calculated although at the time of analysis there was no accepted *Log* K_{pw} value calculated for PDMS using the co-solvent method.

6.1.4 Investigation of the Salting Out Effect

Smedes and Booij [115] report that where silicone rubber PSDs are exposed to marine and estuarine sites the salinity of these waters has an effect on the K_{pw} value of each compound. In many PDMS PSD deployments from the literature [191,173,192] no reference is made as to whether "salting out effects" have been considered in the calculation of the R_s and C_w values where samplers are deployed in marine (salt water) sites. Further, Smedes and Booij [115] indicate that when using *Eqn. 2.7* to calculate the *Log* K_{pw}^{so} value for marine sites the ionic strength of seawater (*I*) using salinity values (35.17 g L^1) at 10 ^oC is used. This gives an "*I*" value of 0.715 mol L^{-1} which can increase the *Log* K_{pw}^{so} value by up to 0.55 log units. Failure to account for such differences can ultimately lead to biased results for marine environments. An investigation into the extent of this effect on pollutant levels is further described below.

6.1.4.1 Determination of Alternative R_s and C_w in Salt Water

As mentioned (section 2.2.4.4) the saline conditions found at inshore marine deployment sites can have an effect on sorption of hydrophobic compounds onto PDMS PSDs hence this affect must be characterised and understood to ensure generation of high quality PS data. POPs such as PAHs and PCBs bind more extensively to solid phases in the marine environment. The so called 'salting out'

effect is driven by the interaction of inorganic salts, found in the water, with the POPs themselves altering their aqueous activity coefficients.[113, 193] Consequently the diffusion of PRCs, spiked into the PSD before the deployment must behave in a similar manner in the marine environment.[119] This effect on PDMS has been studied by both Jonker and Muijis [113] and Smedes and Booij [115] with increases in *Log* K_{pw} values of 0.55 log units reported.

To demonstrate the potential for bias associated with R_s and C_w data the Gweebarra site was chosen as being representative of an average marine (and proposed baseline/reference) site. The partition coefficients (*Log* K_{pw}^{so}) (appendix A.1) used for a marine site were used to calculate 'true' R_s and C_w values (appendix A.9 *Table 1*). The R_s value associated with this deployment were then recalculated using fresh water partition coefficients (*Log* K_{pw}) as per section 4.4.2.2. The Gweebarra salt water R_s was calculated as 36.7 ± 0.75 L/d, while utilising the alternative R_s estimated using fresh water partition coefficients is estimated at 20.6 ± 0.42 L/d. The alternative R_s value calculated using the *Log* K_{pw} fresh water partition coefficients values in a marine site was found to be 56.2 % lower than the salt water equivalent value.

To further illustrate this point *Table 6.1* below shows the original (True) concentrations calculated using the correct *Log* K_{pw}^{so} values and the incorrectly modelled freshwater *Log* K_{pw} values (alternative) for the Gweebarra site. Also shown are the sampling rates and the differences between the two calculations.

It was determined that an overestimation of the final C_w values by 56.2 % would occur at this particular location should the incorrect *Log* K_{pw} values be used in marine deployments and a decrease in the R_s value causes a proportional increase in the C_w value calculated. It can be concluded that correcting *Log* K_{pw} values as was completed in this case for the salting out affect for PSDs deployed in marine conditions is imperative to allow correct estimations of C_w concentrations be made, this being especially pertinent where data are derived for "baseline/reference" sites and for subsequent application in derivation of legislative thresholds.

Table 6.1 True and alternative values of C_w (ng/L) concentrations and R_s (L/d) calculated using fresh and marine (saline) *Log* K_{pw} values.

Compound C_w (ng/L)	TRUE	Alternative
Acenaphthylene	2.80	4.99
Acenaphthene	0.52	0.93
Fluorene	0.10	0.19
Phenanthrene	4.01	7.14
Anthracene	0.60	1.07
Fluoranthene	0.65	1.17
Pyrene	0.37	0.66
Chrysene	0.02	0.03
Benzo(a)anthracene	0.07	0.13
Benzo(b)fluoranthene	0.01	0.01
Benzo(k)fluoranthene	0.01	0.01
Benzo(a)pyrene	0.01	0.02
Indeno(1,2,3-cd)pyrene	0.003	0.005
Dibenzo(a,h)anthracene	0.0005	0.001
Benzo(g,h,i)perylene	0.002	0.004
Rs (L/d)	36.7	20.6

6.1.5 Quality Control of Passive Sampling Data Generation

Where at all possible this study employed a number of QA processes to enhance confidence in analytical data generation, with analysis of PSDs in this study having incorporated the use of blanks, field controls and replicate samplers. Also used for quality assurance of PSDs was the determination of concentrations in PDMS materials previously utilised for the purposes of proficiency testing. The NORMAN network [194] instigated an inter-laboratory study for the analysis of PBDE compounds using a variety of passive samplers in 2011. The study was designed to answer a number of pertinent questions (*e.g* variability in analysis techniques and methods of data generation *etc*.) in relation to PSDs and their potential use in monitoring programmes.[194] The NORMAN proficiency materials while specifically used for the analysis of PBDEs within the framework of the exercise were additionally analysed for PAHs by one other participant (personal communication Ian Allan - NIVA). This PBDE and PAH data were then compared to analysis completed in this chapter (exception M6 data previously reported) thus adding a further QA element to the data reported.

NORMAN proficiency samplers were extracted and analysed in accordance with methods outlined throughout this study. It must be noted that no blank T_0 sheets used to calculate N_t/N_0 values were available therefore it was not possible to estimate C_w concentration for these proficiency materials, however it was possible to quantify contaminants on a per sampler basis.

It is clear from *Table 6.2* that extraction and quantification of PBDEs and PAHs (personal communication Ian Allan - NIVA) in PDMS PSDs is working within the

variability of the NORMAN network study and that data generated for PAHs (ng/sampler) analysed by NIVA are similar, thus indicating that a high level of agreement exists between the analytical methodologies employed in this study and those of other recognised laboratories in the analysis of PDMS membranes.

The fact that these show that membrane concentrations of analytes in this study are within the variability of the NORMAN network study in effect supports data quality in terms of calculation of dissolved pollutant levels once high confidence is assumed in respect of variability in reported *Log* K_{pw} values of analytes. Section 3.5.2.1 details the *Log* K_{pw} values used in this study (Booij and Smedes) [119] these having been calculated using the co-solvent method which eliminates large variability in *Log* K_{pw} estimation. Having incorporated the documented QA procedures and peer-reviewed *Log* K_{pw} values it can be stated that the extraction and estimation of C_w values using passive samplers was deemed to be under control within current guidelines.

Table 6.2 Inter-comparison of average (N=3) results on a membrane (ng/sampler) basis from this study and NORMAN network provided PDMS samplers

Compound (ng/sampler)	This study Average	Norman values Average	Compound (ng/sampler)	This study Average	Norman values Average
PBDE 28	1.16	1.04	Fluoranthene	1,825	1,700
PBDE 47	23.1	19.0	Pyrene	1,520	1,700
PBDE 100	2.55	2.91	Benzo[a]anthracene	208	260
PBDE 99	9.6	9.5	Chrysene	259	350
PBDE 154	0.21	0.28	Benzo[b,j]fluoranthene	55.5	200
PBDE 153	0.21	0.24	Benzo[k]fluoranthene	62.7	74.0
Acenaphthylene	17.4	<10	Benzo[e]pyrene	n.a	140
Acenaphthene	71.2	<50	Benzo[a]pyrene	66.6	77.0
Fluorene	154	150	Perylene	n.a	19.0
Dibenzothiophene	n.a	<120	Indeno[1,2,3-cd]pyrene	22.5	21.0
Phenanthrene	397	490	Dibenzo[a,h]anthracene	10.2	5.20
Anthracene	120	<80	Benzo[ghi]perylene	31.8	42.0

n.a- not applicable

6.2 Results and Discussion

Results for the deployment of passive samplers from sites sampled as part of this study are shown in *Table 6.3.* The influence of site classification and location for each of the parameter groupings (PAHs, PCB, OCs and PBDEs) are further described supported by utilisation of PCA profiling techniques.

Table 6.3 (A) C_w concentrations for PAHs (ng/L) and PCBs (pg/L) using PDMS passive samplers in locations across Ireland.

Location	Mutton	Dublin	Bantry	Omey			Wexford		NWA	Gweebarra	Erne	Furnace		Lower	Upper	Limerick	Upper	New	upper	Nore	Upper	Black	Eel	Lough	Gallaghers	M6 250 M		M6 750 M		M6 1040 M		M6 PDMS PSD			
	Island	Port	Bay	Island	Cork 1	Cork 2	Harbour	Shannon	Seaboard	Bay	Estuary	Lough	Kilkeiran	Shannon	Shannon	Dock	Blackwater	Ross	Barrow	Estuary	Slaney	River	Wier	Bunevella	Lake	SPMD 1	SPMD 2	SPMD 1	SPMD 2	SPMD 1	SPMD 2	5M	250M	750M	1040M
Latitude	53.259257°N	53.345223°N	51.641885°N	53.528677°N	51.837793°N	51.837793°N	52.339849°N	52.689806°N	54.86877°N	54.84115°N	54.50612°N	53.90009°N	53.31804°N	52.63312°N	52.68114°N	52.65645°N	52.14925°N	52.36772°N	52.4881°N	52.485555°N	52.45274°N	53.572004°N	53.553086°N	54.024486°N	53.554078°N	53.07482°N	53.07482°N	53.07482°N	53.07482°N	53.07482°N	53.07482°N	53.07482°N	53.07482°N	53.07482°N	53.07482°N
Longitude	9.041061°W	6.214314°W	9.699554°W	10.168533°W	8.29073°W	8.29073°W	6.457729°W	8.903046°W	8.53792°W	8.46227°W	8.22073°W	9.57333°W	9.72797°W	9.1223°W	8.82172°W	8.66077°W	7.85817°W	6.9661°W	6.932°W	7.06479°W	6.52999°W	9.345059°W	9.344349°W	9.321811oW	9.321811oW	15.88135°W	15.88135°W	15.88135°W	15.88135°W	15.88135°W	15.88135°W	15.88135°W	15.88135°W	15.88135°W	15.88135°W
Year	2010	2010	2010	2010	2010	2010	2010	2010	2012	2012	2012	2012	2012	2012	2012	2012	2012	2012	2012	2012	2012	2009	2009	2009	2009										
Device type	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	SPMD	SPMD	SPMD	SPMD	SPMD	SPMD	PDMS	PDMS	PDMS	PDMS
Water Body type	Saline	Saline	Saline	Saline	Saline	Saline	Saline	Saline	Saline	Saline	Fresh	Transitional	Saline	Transitional	Transitional	Fresh	Fresh	Fresh	Fresh	Fresh	Fresh	Fresh	Fresh	Fresh	Fresh	Marine	Marine	Marine	Marine	Marine	Marine	Marine	Marine	Marine	Marine
Site description	Marine	Estuary	Marine	Marine	Estuary	Estuary	Estuary	Estuary	Marine	Marine	Esutary	River	Marine	Esutary	Esutary	Esutary	Esutary	River	River	Esutary	River	Lake	Lake	Lake	Lake	Ocean	Ocean	Ocean	Ocean	Ocean	Ocean	Ocean	Ocean	Ocean	Ocean
Code	MI(M)	DP(E)	BB(M)	OI(M)	CI(E)	C2(E)	WH(E)	Sh(E)	NWA(M)	GB(M)	EE(E)	FL(R)	Kil(M)	LS(E)	Ush(E)	LD(E)	UB(E)	NR(R)	UB(R)	NE(E)	US(R)															
Compound ng/L																									Compound pg/L^{-1}										
Acenaphthylene	0.77	3.24	1.36	0.30	1.11	0.85	1.70	1.61	0.10	2.80	0.66	0.61	0.16	2.69	5.62	4.58	0.84	3.50	0.80	1.54	0.86	5.28	4.36	3.93	5.14	32.0	41.0	34.8	23.9	28.8	33.0	37	5.56	4.22	2.89
Acenaphthene	0.33	2.64	0.57	0.14	2.02	1.37	4.32	1.13	0.03	0.52	0.18	0.43	0.05	3.73	6.20	8.03	1.35	1.85	0.61	0.84	0.85	1.71	1.22	1.29	1.85	21.6	22.8	16.7	14.6	14.5	11.7	42	7.54	4.20	3.54
Fluorene	0.91	4.12	2.85	0.67	5.32	3.90	3.12	4.50	0.08	0.10	0.30	0.71	0.04	3.37	3.63	2.59	0.91	2.25	2.75	1.01	0.49	4.51	5.86	5.30	7.26	60.7	64.5	52.5	51.3	44.2	42.6	50	20.40	11.20	10.90
Phenanthrene	2.08	4.85	2.88	1.27	9.48	8.67	4.67	12.4	2.13	4.01	17.2	3.03	5.66	6.22	7.44	10.8	16.2	16.0	16.9	19.2	6.6	10.2	16.6	14.1	13	176	184	174	162	133	143	406	308	328	210
anthracene	0.16	0.89	0.16	0.05	0.48	0.63	1.26	0.70	1.02	0.60	5.75	0.11	0.23	1.20	1.08	0.41	0.49	3.56	1.90	3.43	4.35	0.31	0.80	0.19	0.31	11.0	12.4	11.6	10.9	9.6	10.8	10	16.50	19.20	10.90
Fluoranthene	1.02	5.47	0.66	0.52	5.60	4.98	5.45	5.97	0.50	0.65	5.76	1.24	1.87	2.65	3.01	6.25	4.30	4.93	6.45	4.64	3.67	3.06	15.60	9.60	3.72	22.8	22.7	91.7	87.1	65.9	83.3	39	37.50	95.60	78.90
Pyrene	0.56	6.10	0.26	0.10	3.39	3.07	3.32	3.43	0.16	0.37	3.58	0.77	0.84	2.49	2.63	4.40	2.47	4.13	3.70	3.16	4.88	1.71	8.84	6.05	2.56	5.7	5.3	14.9	14.3	11.8	15.4	14	6.16	10.80	8.68
Chrysene	0.06	1.09	0.01	0.02	0.47	0.41	0.75	0.19	0.01	0.02	0.30	0.07	0.06	0.16	0.31	0.62	0.19	0.79	0.53	0.20	0.04	0.14	1.23	1.12	0.30	2.4	2.4	2.6	2.5	1.9	2.2	1.5	0.73	0.65	0.40
Benzo(a)anthracene	0.12	1.64	0.05	0.04	1.17	1.06	1.43	0.57	0.03	0.07	0.51	0.12	0.11	0.15	0.25	0.65	0.27	0.64	0.38	0.28	0.06	0.38	4.86	3.23	0.92	10.3	9.7	23.7	22.7	18.0	24.8	4.9	5.39	10.50	7.46
Benzo(b)fluoranthene	0.04	0.89	0.02	0.02	0.76	0.67	0.88	0.11	0.01	0.01	0.07	0.02	0.01	0.03	0.07	0.12	0.03	0.22	0.05	0.03	0.01	0.14	3.28	1.65	0.29	6.7	6.2	9.9	7.3	9.6	13.9	3.2	3.53	3.90	1.37
Benzo(k)fluoranthene	0.03	0.54	0.02	0.02	0.76	0.64	0.77	0.11	0.004	0.01	0.11	0.04	0.02	0.05	0.11	0.19	0.04	0.29	0.08	0.10	0.01	0.13	2.16	1.16	0.26	3.6	3.4	4.2	3.3	3.9	4.6	2.4	2.70	3.17	1.34
Benzo(a)pyrene	0.02	0.67	0.005	0.01	0.28	0.22	0.19	0.04	0.003	0.01	0.06	0.04	0.01	0.03	0.06	0.14	0.02	0.18	0.03	0.04	0.01	0.06	0.49	0.35	0.16	0.7	0.6	0.5	0.5	0.5	0.6	5.2	1.73	0.06	0.97
Indeno(1,2,3-cd)pyrene	0.01	0.19	0.01	0.01	0.47	0.31	0.18	0.03	0.003	0.003	0.06	0.02	0.01	0.01	0.03	0.07	0.02	0.11	0.04	0.03	0.07	0.09	0.89	0.48	0.22	0.3	0.1	0.3	0.1	0.4	0.8	0.6	0.15	0.02	0.08
Dibenzo(a,h)anthracene	0.01	0.07	0.001	0.003	0.11	0.05	0.04	0.003	0.0005	0.0005	0.01	0.003	0.0002	0.003	0.01	0.005	0.02	0.01	0.005	0.01	0.01	0.06	0.30	0.16	0.13	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	0.08	<0.001	<0.003	<0.004
Benzo(g,h,i)perylene	0.01	0.24	0.003	0.004	0.39	0.27	0.14	0.03	0.002	0.002	0.09	0.02	0.01	0.02	0.04	0.09	0.03	0.13	0.03	0.02	0.10	0.06	0.58	0.35	0.23	0.27	<0.01	0.28	0.16	<0.01	0.26	0.48	0.32	0.23	0.1
SUM	6.11	32.7	8.86	3.18	31.8	27.1	28.2	30.9	4.07	9.19	34.6	7.23	9.07	22.8	30.5	38.9	27.2	38.5	34.3	34.5	22.0	27.8	67.1	49.0	36.3	354	375	438	401	342	388	616	416	492	338
p/A	12.8	5.43	17.6	23.5	19.7	13.7	3.72	17.8	2.08	6.65	2.99	28.3	24.2	5.19	6.91	26.5	33.0	4.49	8.92	5.60	1.52	32.9	20.9	74.2	41.9	15.99	14.85	14.96	14.94	13.96	13.33	39.80	18.67	17.08	19.27
fl/Py	1.83	0.90	2.52	5.12	1.65	1.62	1.64	1.74	3.08	1.77	1.61	1.61	2.23	1.07	1.14	1.42	1.74	1.20	1.74	1.47	0.75	1.79	1.76	1.59	1.45	4.0	4.3	6.2	6.1	5.6	5.4	2.8	6.1	8.9	9.1
LPAH/HPAH	2.27	0.93	7.52	3.27	1.38	1.32	1.15	1.94	4.65	7.05	2.28	2.08	2.09	3.08	3.69	2.11	2.68	2.38	2.03	3.06	1.49	3.77	0.76	1.02	3.13	5.7	6.4	2.0	1.9	2.1	1.7	6.7	4.8	2.5	2.2
Compound pg/L																																			
PCB 18	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	9.01	17.5	19.8	n.a*	1.59	20.6	182	290	34.5	268	111	209	128	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	0.39	0.34	0.89	0.49
PCB 31	<0.18	<0.5	<0.1	<0.42	<0.84	<0.84	<0.19	<0.16	9.6	12.0	19.7	20.7	1.04	4.91	21.1	81.7	9.8	37.1	6.06	12.6	11.3	n.a*	n.a*	n.a*	n.a*	0.99	0.87	0.52	0.55	0.65	0.56	0.41	0.34	0.57	0.36
PCB 28	<0.08	<2.2	<0.4	<1.8	<3.6	<3.6	<0.8	<0.7	21.5	8.00	46.8	10.2	1.68	10.0	20.6	94.4	28.2	71.0	31.1	21.9	41.3	20.1	100	240	293	0.72	0.62	1.19	1.82	0.65	1.00	0.41	0.38	0.56	0.28
PCB 52	n.d	n.d	3.97	n.a*	167	170	n.a*	31.8	4.11	2.56	6.81	13.7	0.85	6.53	27.4	71.7	16.8	50.7	7.46	11.0	22.3	n.a*	n.a*	n.a*	n.a*	0.97	1.04	1.63	1.58	0.88	0.76	0.19	0.29	0.88	0.40
PCB 44	<0.12	<0.4	<0.06	<0.32	73.5	69.4	<0.13	39.0	3.45	6.62	27.4	4.91	0.49	5.93	17.9	53.4	15.5	37.5	5.64	8.05	34.3	n.a*	n.a*	n.a*	n.a*	0.95	0.87	1.21	1.59	0.29	0.16	0.11	0.25	0.85	0.25
PCB 101	n.a*	n.a*	n.a*	n.a*	129	116	n.a*	n.a*	5.41	7.92	11.0	3.62	0.63	9.09	28.8	52.7	10.9	38.4	5.37	4.42	11.0	101	293	320	462	0.31	0.29	0.52	0.40	0.42	0.36	0.16	0.38	0.38	0.25
PCB 149	3.96	94.7	<0.05	8.30	98.8	110	116	<0.11	2.78	1.36	6.00	2.98	0.33	4.95	13.4	17.8	4.57	28.1	1.03	5.81	5.42	5.84	39.2	10.4	33.6	n.d	n.d	n.d	n.d	n.d	n.d	0.12	0.21	0.31	0.15
PCB 118	27.4	215	13.3	84.7	148	115	29.0	23.3	5.07	10.2	4.23	2.05	2.03	5.62	20.3	24.1	3.59	46.8	6.97	13.2	14.5	84.8	312	318	474	0.63	0.59	1.52	1.71	0.56	0.54	0.24	0.16	0.16	0.26
PCB 153	53.1	262	17.1	148	141	153	34.5	41.9	3.78	33.6	45.1	12.9	4.46	7.92	20.5	34.0	6.27	25.7	8.72	12.2	17.3	110	537	471	605	0.91	0.94	1.89	1.99	1.79	1.90	0.22	0.44	0.27	0.29
PCB 105	9.02	44.3	1.28	146	3.36	3.33	74.8	<0.50	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	42.8	90.5	136	112	0.25	0.26	0.74	0.81	0.10	0.07	0.34	0.75	0.80	0.28
PCB 138	28.4	139	10.6	113	151	143	32.9	43.4	1.28	13.1	7.45	3.64	1.20	7.45	14.7	17.2	3.03	13.3	3.05	5.25	3.53	59.9	453	407	574	0.44	0.42	1.06	1.21	0.65	0.55	0.56	0.42	0.25	0.15
PCB 156	2.42	15.7	<0.11	12.6	69.1	135	48.8	110	1.44	3.00	2.46	10.5	0.20	2.05	1.43	1.99	0.29	0.81	0.51	0.64	0.47	n.d	n.d	n.d	n.d	0.12	0.14	0.23	0.55	0.05	0.04	0.02	0.09	0.30	0.05
PCB 180	11.2	225	5.45	23.7	118	123	28.3	16.7	3.39	1.55	4.11	4.03	0.51	4.68	7.06	10.3	0.71	6.03	1.49	3.56	3.93	41.4	152	102	293	0.14	0.14	0.34	0.37	0.28	0.30	0.11	0.10	0.09	0.07
PCB 170	<0.31	12.4	3.23	2.98	20.9	38.1	52.8	4.16	0.33	0.20	<0.10	0.73	<0.06	0.44	1.37	1.24	0.68	1.12	<0.09	0.11	<0.23	n.d	n.d	n.d	n.d	0.06	0.07	0.13	0.15	0.08	0.07	0.03	0.07	0.01	0.02
PCB 194	1.63	61.9	3.09	2.81	<2.82	n.a*	<0.53	114	<0.16	1.49	<0.30	<0.30	<0.16	<0.09	0.61	<0.35	<0.35	<0.25	<0.25	0.26	<0.72	40.8	198	144	241	K	K	K	K	K	K	<0.03	0.13	0.02	0.02
PCB 209	0.69	38.9	<0.21	<1.32	<2.76	<2.76	<0.51	<0.42	0.49	1.01	1.01	<0.42	<0.22	2.43	1.53	3.78	1.00	1.38	<0.35	<0.36	<1.01	n.d	n.d	n.d	n.d	K	K	K	K	K	K	0.003	0.24	0.15	0.09

n.d – not detected , n.a – not analysed, n.a* – analytical interfence in chromatogram. K – sampler concentration calculated but no *Log* K_{pw} value

Table 6.3 (B) C_w concentrations for OCs (ng/L) and BFRs (pg/L) using PDMS passive samplers in locations across Ireland.

Location	Mutton	Dublin	Bantry	Omey			Wexford		NWA	Gweebarra	Erne	Furnace		Lower	Upper	Limerick	Upper	New	upper	Nore	Upper	Black	Eel	Lough	Gallaghers	M6 250 M		M6 750 M		M6 1040 M		M6 PDMS PSD			
	Island	Port	Bay	Island	Cork 1	Cork 2	Harbour	Shannon	Seaboard	Bay	Estuary	Lough	Kilkeiran	Shannon	Shannon	Dock	Blackwater	Ross	Barrow	Estuary	Slaney	River	Wier	Bunevella	Lake	SPMD 1	SPMD 2	SPMD 1	SPMD 2	SPMD 1	SPMD 2	5M	250M	750M	1040M
Latitude	53.259257°N	53.345223°N	51.641885°N	53.528677°N	51.837739°N	51.837793°N	52.339849°N	52.689806°N	54.868777°N	54.84115°N	54.50612°N	53.90009°N	53.31804°N	52.63312°N	52.68114°N	52.65645°N	52.14925°N	52.36772°N	52.4881°N	52.48555°N	52.45274°N	53.572004°N	53.553086°N	54.024486°N	53.554078°N	53.07482°N	53.07482°N	53.07482°N	53.07482°N	53.07482°N	53.07482°N	53.07482°N	53.07482°N	53.07482°N	53.07482°N
Longitude	9.041061°W	6.214314°W	9.699554°W	10.168533°W	8.29073°W	8.29073°W	6.457729°W	8.903046°W	8.53792°W	8.4627°W	8.22073°W	9.57333°W	9.77297°W	9.1223°W	8.82172°W	8.66077°W	7.85817°W	6.9661°W	6.932°W	7.06478°W	6.52999°W	9.345059°W	9.344349°W	9.321811oW	9.321811oW	15.88135°W	15.88135°W	15.88135°W	15.88135°W	15.88135°W	15.88135°W	15.88135°W	15.88135°W	15.88135°W	15.88135°W
Year	2010	2010	2010	2010	2010	2010	2010	2010	2012	2012	2012	2012	2012	2012	2012	2012	2012	2012	2012	2012	2012	2009	2009	2009	2009										
Device type	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	SPMD	SPMD	SPMD	SPMD	SPMD	SPMD	PDMS	PDMS	PDMS	PDMS
Water Body type	Saline	Saline	Saline	Saline	Saline	Saline	Saline	Saline	Saline	Saline	Fresh	Transitional	Saline	Transitional	Transitional	Fresh	Fresh	Fresh	Fresh	Fresh	Fresh	Fresh	Fresh	Fresh	Fresh	Marine	Marine	Marine	Marine	Marine	Marine	Marine	Marine	Marine	Marine
Site description	Marine	Estuary	Marine	Marine	Estuary	Estuary	Estuary	Estuary	Marine	Marine	Esutary	River	Marine	Esutary	Esutary	Esutary	Esutary	River	River	Estuary	River	Lake	Lake	Lake	Lake	Ocean	Ocean	Ocean	Ocean	Ocean	Ocean	Ocean	Ocean	Ocean	Ocean
Code	MI(M)	DP(E)	BB(M)	OI(M)	C1(E)	C2(E)	WH(E)	Sh(E)	NWA(M)	GB(M)	EE(E)	FL(R)	Kil(M)	LS(E)	Ush(E)	LD(E)	UB(E)	NR(R)	UB(R)	NE(E)	US(R)														
Compound ng/L																																		
α-HCH	1.77	1.74	0.73	0.51	5.52	5.39	4.87	8.12	2.38	<0.01	5.02	4.02	0.13	2.60	4.18	7.62	2.04	1.83	6.74	3.62	1.74	3.32	2.91	2.36	0.66	32.9	34.7	46.1	56.6	36.1	34.7	143	104	89	72.5
β-HCH	2.84	7.13	3.43	0.004	3.73	3.47	2.10	n.a*	n.a*	n.d	n.d	n.d	0.07	3.05	4.68	0.56	1.12	n.d	n.d	4.12	0.99	3.40	2.09	3.11	<0.02	n.d	n.d	n.d	n.d	n.d	n.d	267	265	173	149
Endosulphane sulphate	0.01	0.67	0.001	0.002	0.40	0.39	0.13	0.27	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	26.9	30.7	41.0	26.4	28.4	n.d	n.a*	n.a*	n.a*	n.a*
Lindane	1.35	10.4	2.22	0.09	6.17	6.09	6.09	6.12	2.61	0.03	3.99	3.47	0.04	2.94	3.66	4.70	3.01	2.74	4.34	2.58	0.78	2.64	1.34	1.17	1.22	34.8	35.3	22.8	11.5	31.5	71.4	n.d	n.d	n.d	n.d
op-DDD	0.05	0.45	0.03	0.04	0.49	0.45	0.04	0.15	0.0003	0.0001	0.01	0.001	0.001	0.03	0.01	0.20	0.01	0.02	0.03	0.02	0.06	0.004	n.d	n.d	n.d	0.05	0.06	0.80	0.74	0.43	0.37	n.d	n.d	n.d	n.d
op-DDT	0.05	0.49	0.08	0.45	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.23	1.12	0.65	0.54	1.31	1.86	3.70	4.98	3.52	4.25	<0.02	0.36	0.05	<0.02
pp-DDD	0.003	0.11	0.02	0.11	0.91	0.92	0.46	0.50	0.0003	<0.30	0.05	0.001	0.004	0.03	0.18	0.06	0.08	0.05	0.21	0.11	0.36	<0.46	<0.01	<0.01	<0.01	0.44	0.43	2.55	3.02	1.01	1.13	5.37	3.07	1.42	1.38
pp-DDE	0.09	0.34	0.003	0.12	0.36	0.41	0.08	0.05	0.001	0.20	0.04	0.001	0.001	0.04	0.09	0.15	0.03	0.02	0.13	0.09	0.27	0.06	0.24	0.30	0.27	0.98	1.10	4.36	4.96	2.72	4.15	0.09	0.18	0.28	0.15
pp-DDT	0.0003	0.06	0.01	0.04	1.47	1.58	0.13	0.33	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.20	0.94	0.31	0.10	1.88	1.99	7.08	8.84	6.23	7.83	2.19	0.50	0.79	2.19
Trans chlordane	<0.001	<0.003	0.013	0.02	0.97	0.86	0.19	0.20	0.001	<0.0003	0.98	0.001	0.001	0.03	0.001	0.08	0.004	<0.07	0.003	0.0004	0.004	0.04	0.05	0.13	0.11	0.91	1.13	1.68	1.94	1.25	2.30	n.d	n.d	n.d	n.d
op-DDE	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.0004	0.0002	0.003	0.0003	0.0009	0.01	0.02	0.06	0.001	0.0004	0.002	0.0003	0.002	n.d	n.d	n.d	n.d	0.33	0.50	3.77	4.77	4.21	2.57	0.64	0.32	0.12	0.15
cis-chlordane	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.002	n.d	0.01	0.01	0.004	0.01	0.01	0.004	0.01	0.0004	0.001	0.01	0.02	0.001	0.003	0.14	0.001	1.39	1.65	4.56	4.79	2.32	2.59	0.40	0.68	0.52	0.16
Dieldrin	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.002	0.0001	0.07	0.05	0.02	0.03	0.12	0.21	0.35	0.86	0.51	0.57	1.19	0.063	0.097	0.361	0.68	4.96	4.65	33.7	78.1	52.3	28.7	2.10	1.36	2.33	1.13
HCB	0.12	n.a*	0.03	n.a*	0.20	0.20	0.06	0.12	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	0.03	0.05	0.03	0.01	12.1	12.3	16.2	19.0	13.0	15.2	0.14	0.25	0.32	0.86
Heptachlor	n.a*	n.a*	n.a*	n.a*	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	0.68	0.75	0.85	2.34	0.52	2.74	K	K	K	K
Oxychlordane	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	21.0	21.1	12.0	34.7	73.2	35.5	K	K	K	K
Heptachlor Epoxide	n.a*	n.a*	n.a*	n.a*	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	9.7	7.37	5.48	7.47	4.09	3.23	K	K	K	K
Trans-Nonachlor	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	0.75	0.80	0.49	0.55	7.11	7.39	K	K	K	K
Endosulfan	0.006	0.669	0.001	0.002	0.395	0.385	0.128	0.272	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	n.a*	26.6	26.9	30.7	41.0	26.4	28.4	n.a*	n.a*	n.a*	n.a*
Endrin	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	10.3	11.1	15.9	16.5	9.6	12.5	K	K	K	K
Compound pg/L																																		
BDE 28	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	0.09	2.04	0.83	2.08	2.17	0.80	<0.06	2.59	2.21	3.02	6.09	7.75	6.87	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a
BDE 47	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	0.81	3.26	7.06	1.34	4.31	6.72	22.1	31.2	24.3	38.7	26.0	46.0	46.8	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a
BDE 100	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	<0.70	0.78	1.96	<1.35	1.37	2.03	5.91	5.94	2.82	7.18	5.98	7.18	10.4	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a
BDE 99	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	1.10	1.96	3.39	0.76	0.74	2.49	8.45	20.6	<6.58	15.1	3.47	19.0	10.7	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a
BDE 154	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	0.66	<0.59	<1.19	<1.18	0.80	0.51	<0.64	<1.37	3.93	1.07	1.95	2.21	3.54	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a
BDE 153	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	<0.98	<0.94	<1.90	<1.90	<0.99	<0.58	<1.03	<2.19	n.a*	1.77	8.45	3.29	<4.60	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a

n.d – not detected , n.a – not analysed, n.a* – analytical interfence in chromatogram. K – sampler concentration calculated but no *Log* K_{pw} value

6.2.1 Evaluation of PAH C_w Concentrations from Irish Waters

Concentrations of PAHs found in PDMS samplers (*Table 6.3*) from across Ireland were found to vary according to location and water salinity with the highest $\sum PAH_{15}$ detected at locations with greater industrial activity and/or marine traffic including Dublin (32.7 ng/L), Cork (31.8 – 27.1 ng/L Cork 1 and 2) and Wexford Harbour (28.2 ng/L). Lowest levels were detected at the Omey Island reference/control site (3.2 ng/L) and at other locations such as North Western Atlantic Seaboard (4.07 ng/L) and Kilkieran (9.07 ng/L) which is consistent with their remote location and lack of industrial activity. These lower level sites can thus be considered as being potential background reference sites for ongoing monitoring.

Concentrations ranged from 3.2 – 39 ng/L from across all sites and are generally low in all water compartments in comparison to those reported by Prokes *et al.* [191] where average $\sum PAH_{16}$ concentrations (including naphthalene) from PDMS samplers at five sites in the Zlin district in the Czech Republic ranged from 47.8 – 93.2 ng/L. Monteyne *et al.* [173] estimated $\sum PAH_{15}$ in PDMS samplers ranged from 3.9 – 170 ng/L at sites in three Belgian coastal harbours while Smedes reported average levels of $\sum PAH_{13}$ between 3.5 – 16.8 ng/L at a site in the Netherlands. [89]

There were major contributions to $\sum PAH_{15}$ from phenanthrene, fluoranthene and pyrene, this pattern compares well with other studies of this nature previously mentioned (from Monteyne [173] and Prokes [191]) as well as other studies from Smedes [89], Emelogu [192] and O'Hara.[123] The lower molecular weight compounds (LPAH:3 – 4

ring compounds) contributed an average of 98 % of the total $\sum PAH_{15}$ which is similar to values reported by Emelogu *et al.* [192] where 5 and 6 ring compounds comprised < 5% of the total $\sum PAH_{40}$. The Ratio ∑LPAH/HPAH data from *Table 6.3* and chapter 4 (*Table 4.10*) was plotted against the $\sum PAH_{15}$ as shown in *Figure 6.1*. This indicates that the source of PAHs from sampled locations across Ireland is predominantly petrogenic in origin. At Dublin, Cork and Wexford (∑HPAHs contributes ~ 8 % of total $\sum PAH_{15}$) pyrogenic influences *i.e* the burning of oils and other fossil fuels, are also observed, this being consistent with the fact that these are among (apart from Wexford Harbour) the biggest ports in Ireland with large volumes of marine traffic.

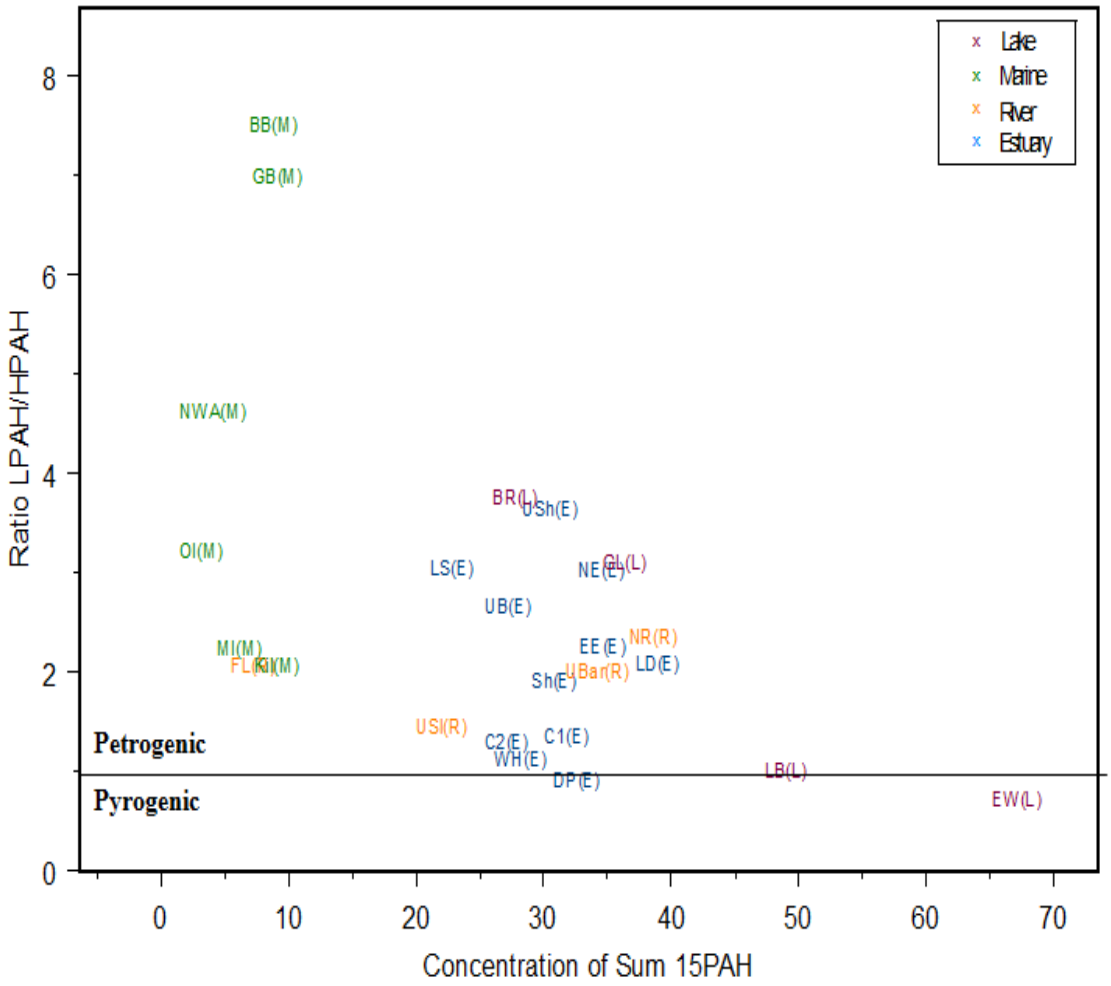


Figure 6.1 PAH profiling using the ratio of the ∑LPAH/HPAH to concentration (ng/L) for all sampled sites from across Ireland

Fluoranthene, pyrene and chrysene as well as the heavier 5 ring compounds like benzo(b)fluoranthene are noted to be present at higher levels in these sites (Dublin, Cork and Wexford) compared with the other sampled sites. Once again the greater contribution of these compounds to the total $\sum PAH_{15}$ indicates a pyrogenic influence at these locations.[20] *Figure 6.1* also shows that the marine sites (labelled in green) are also much lower, concentration wise, than the other sites. The two lake sites (eel weir – EW and Lough Bunevella – LB) show the highest concentrations present in relation to the other sites, this is primarily because as part of the first deployments of passive samplers they may be over-estimated. The Furnace Lough sampler (*Table 6.3*) gives a more accurate estimation of C_w values for this area.

6.2.1.1 PCA Evaluation of PAH

Principal component analysis was completed on a concentration independent basis using the percentage contribution of individual PAHs relative to the $\sum PAH_{15}$ using data from all sites sampled in this study including the M6 weather buoy, and the PCA process previously documented in chapter 4 (section 4.5). *Figures 6.2* and *6.3* show that coastal marine and oceanic profiles generally differ from those in freshwater and estuarine environments, this being evident graphically as samplers from the marine sites NWA, Kilkieran, Gweebarra and Bantry Bay are geographically separated from those in other locations.

It is also evident that replicate samplers in Cork (C1 and C2) behave similarly as do replicate samplers from the M6 offshore weather buoy site. Loading plots indicate

that phenanthrene is the key contributor to the profiles in coastal and offshore samplers while fluoranthene and pyrene are larger contributors to the profiles in more industrial/higher population areas.

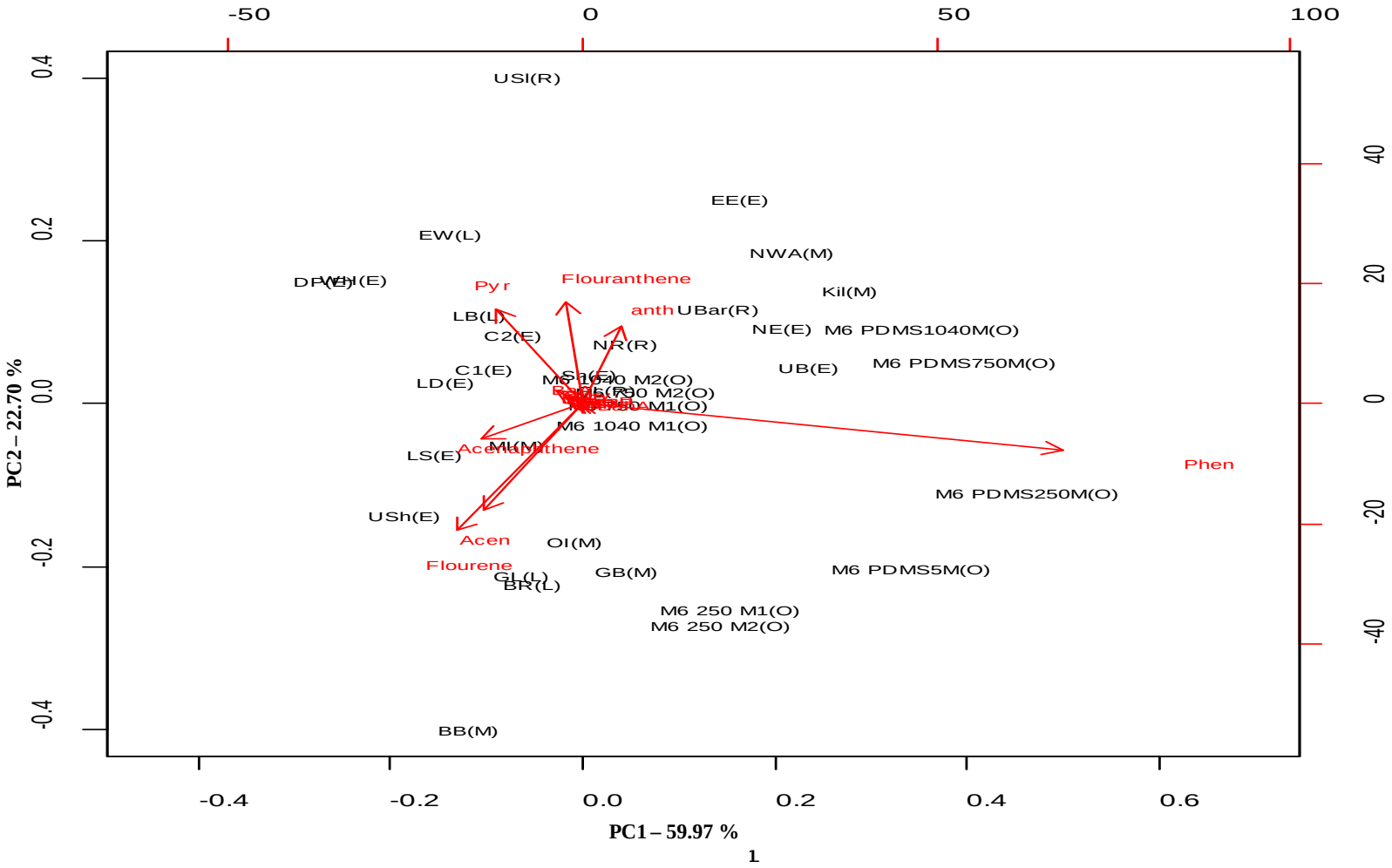


Figure 6.2: PCA plot (PC1 vs PC2) of concentration independent PAH profiles for all sites. Letters in parenthesis indicate WB designation/type; O= Ocean, M=Marine, E = Estuary, L= Lake and R = Riverine.

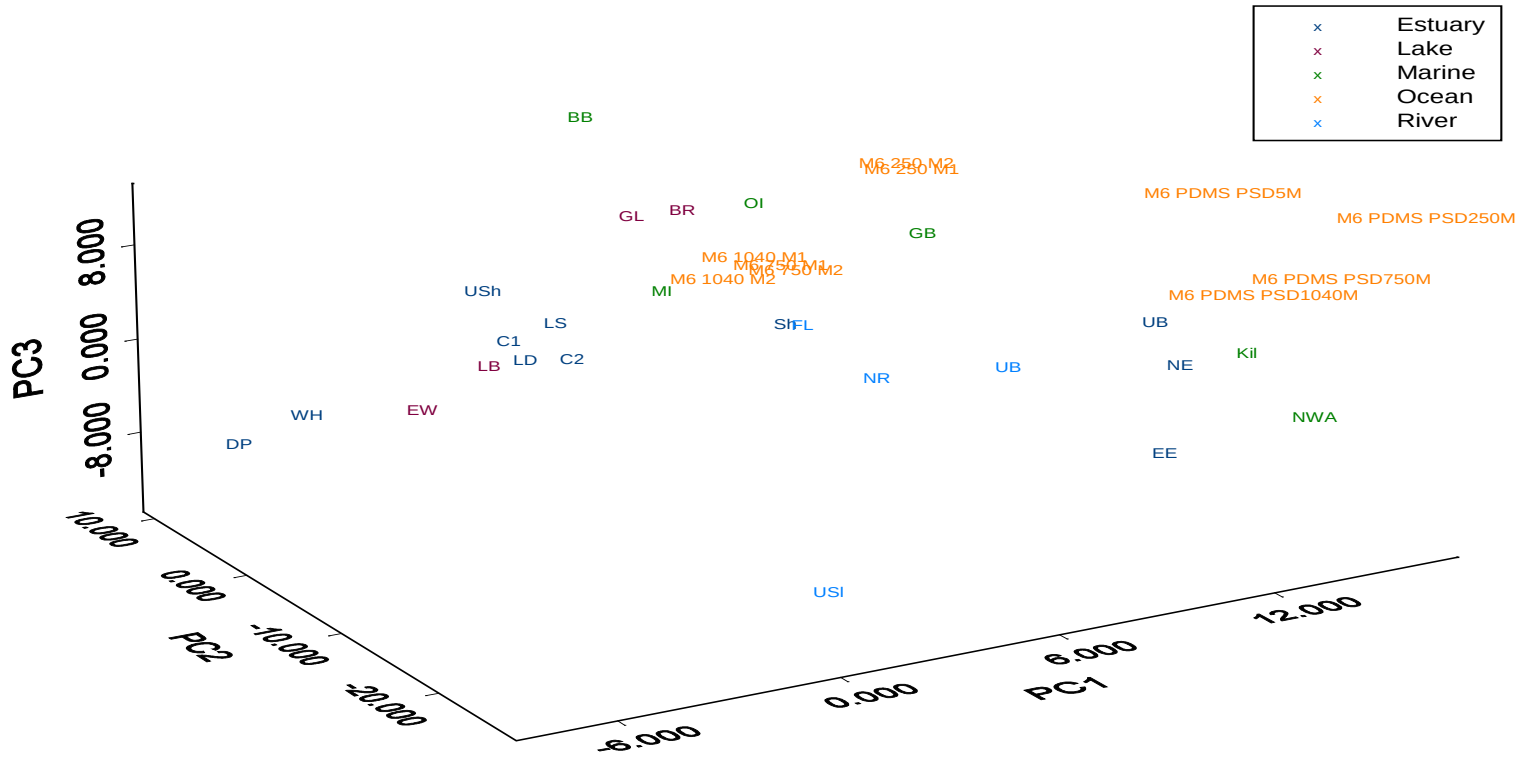


Figure 6.3: 3D PCA plot (PC1 vs PC2 vs PC3) of concentration independent PAH profiles for all sites and WB designation/types (PC1 – 60.01 %, PC2-23.71 %, PC3 – 16.28 %).

6.2.2 Evaluation of PCB C_w Concentrations from Irish Waters

Overall the levels of PCBs found in PSDs from all Irish water body types (as presented in *Table 6.3)* are low (pg/L) in comparison to the levels of PAHs and some OCs. The $\sum PCB_{16}$ ranged from 0.01 ng/L at the remote Kilkieran site to 1.35 ng/L as measured in the replicate Cork (Cork2) sampler. These values are low compared to those of Monteyne *et al.* [173] where the $\sum PCB_{15}$ ranged from 0.3 – 3.1 ng/L in three Belgian coastal harbours and similar to those of Prokes *et al.* [191] who report the average $\sum PCB_7$ concentrations from PDMS samplers in the Zlin district in the Czech republic ranging from 0.17 – 0.48 ng/L. Smedes reports the average levels of $\sum PCB_{14}$ from the Netherlands ranged from 0.05 – 0.35 ng/L.[89] The results reported in *Table 6.3* are high in comparison to those reported by Emelogu *et al.* [192] where $\sum PCB_{32}$ ranged from 0.02 – 0.06 ng/L however, the area sampled by Emelogu, the Ythan catchment in the North east of Scotland, is remote and sparsely populated with little in the way of industry, thus comparisons can be drawn with these data and upperbound data from Kilkieran (0.01 ng/L) or the North Western Atlantic seaboard sites (0.06 ng/L).

Lower contributions to the $\sum PCB_{16}$ were determined for PCBs 18, 28, 52 concurring with the findings of Emelogu *et al.* [192] and Prokes *et al*. [191] The levels of ∑PCBs reported by O'Hara [123] from Dublin (1.5 ng/L) and Galway (0.02 ng/L) are similar to those subsequently measured from similar sites used in this study (1.11 and 0.14 ng/L) for Dublin Bay and Mutton Island, Galway respectively.

6.2.2.1 PCA Evaluation of PCB Concentrations

Concentration independent PCA analysis (*Figure 6.4 and 6.5*) using the percentage contribution of individual PCBs relative to the upperbound $\sum PCB_7$ supports that coastal marine and oceanic profiles generally differ from those in freshwater and estuarine environments, this being evident graphically as samplers from the marine and Oceanic sites are geographically separated from those in other locations (apart from NWA). As per the PAHs it is clear that replicate samplers in Cork (C1 and C2) behave similarly as do replicate samplers from the M6 offshore weather buoy site.

The main driver for the marine and oceanic sites was found to be PCBs 153 and 52 whereas most of the riverine and estuarine sites were influenced by the concentrations of PCBs 118, 138 and 180. A 3D plot of the first three PC as presented in *Figure 6.5* further indicates the statistical separation of marine/coastal sites in the west of Ireland from other locations.

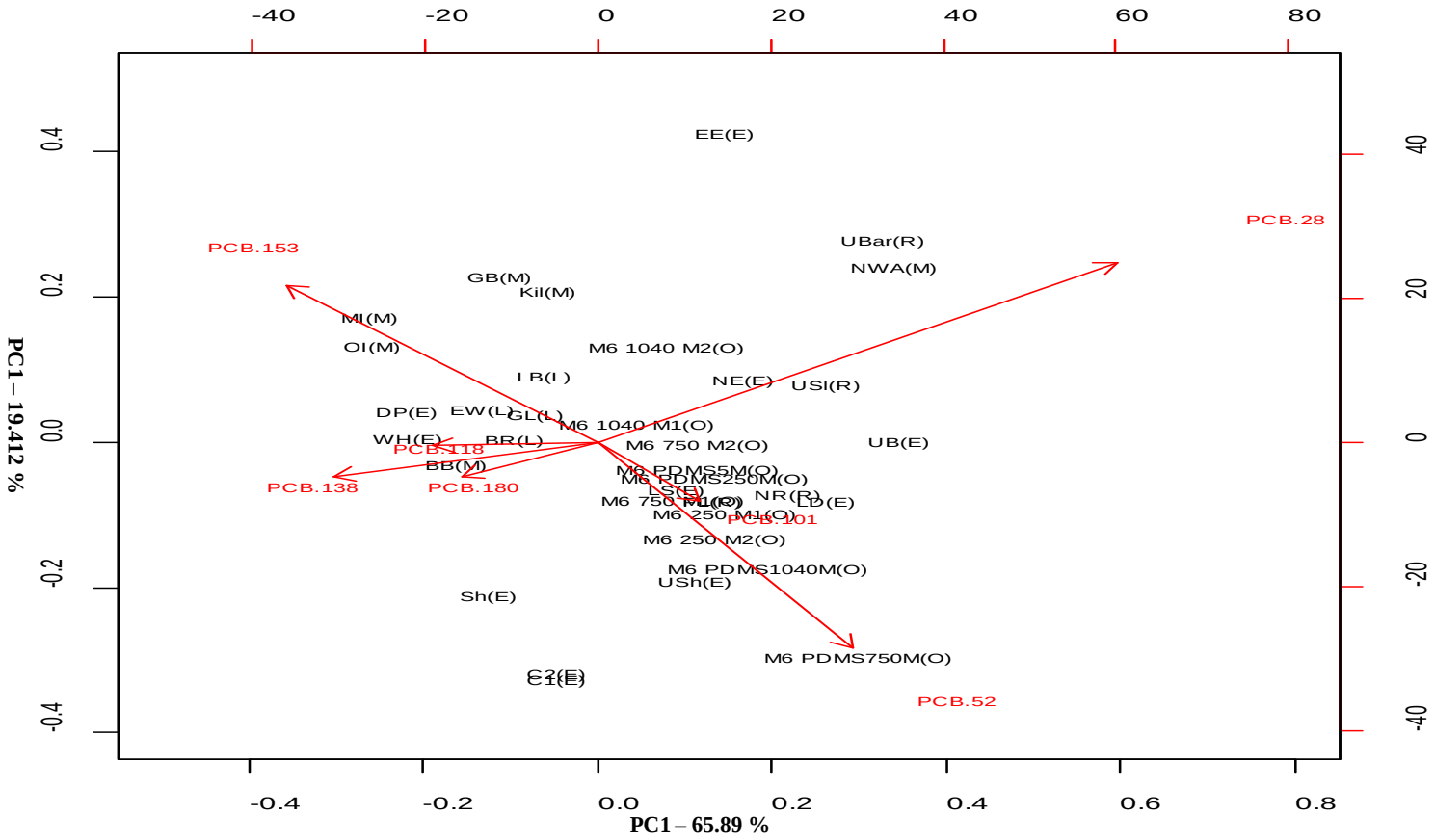


Figure 6.4: PCA plot (PC1 vs PC2) of concentration independent PCB profiles for all sites. Letters in parenthesis indicate WB designation/type; O = Ocean, M =Marine, E = Estuary, L= Lake and R = Riverine.

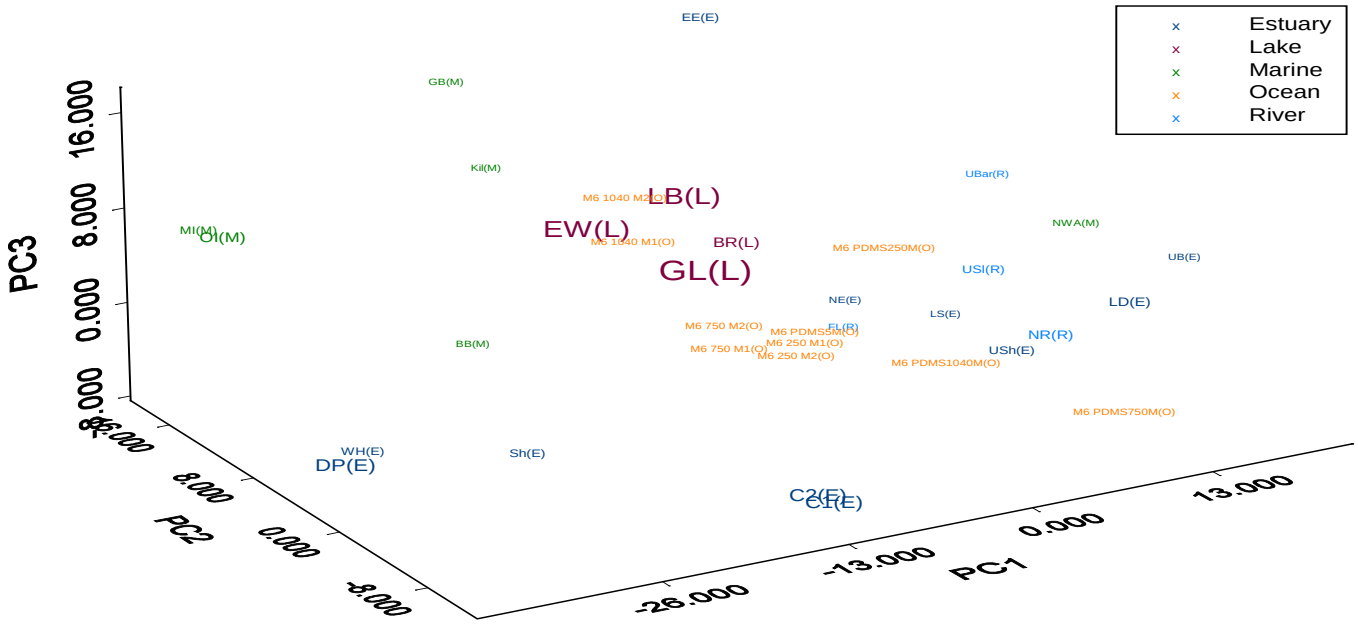


Figure 6.5: 3D PCA plot (PC1 vs PC2 Vs PC3) of concentration independent PCB profiles (based on sum 7 PCBs) for all sites and WB designation/types (PC1 – 65.89 %, PC2 – 19.41 %, PC3 – 16.49 %).

6.2.3 Assessment of OC C_w Concentrations from Irish Waters

OC compounds were generally found to be low in all samplers analysed. It was possible to further evaluate the relative contribution of the upperbound sum of 7 representative OC compounds for each of the sites (*Figure 6.6*). It should be noted that for a number of these sites (especially those on the west coast) upperbound values have been utilised for some compounds, However, where used these do not generally bias the evaluation process as the upperbound limit of reporting was generally of the order of 0.02 ng/L thus contributing to a relatively small percentage contribution to the overall pollutant burden.

OC levels from samplers located at the remote Kilkieran and Gweebarra locations (0.247 and 0.56 $\sum OC_7$ ng/L) were found at lower levels than reported for the Dublin and in the duplicate Cork samplers (20.2 and 18.2 $\sum OC_7$ ng/L) respectively. Overall the major contribution to the overall OC pollutant burden was from the hexachlorocyclohexanes (α, β and γ – HCH) with these compounds dominating the profile in most instances contributing approximately 80% of the total OC pollutant burden, this being in agreement to the study by Prokes *et al.* [191] where ∑HCHs were found to contribute ~ 95 % to the total ∑PCB + OCs reported.

It must be noted that given the low levels of some OCs (especially at more remote locations) the low level occurrence of any one OC compound can correspondingly dramatically alter the PCA profile for that particular site and thus it is important to

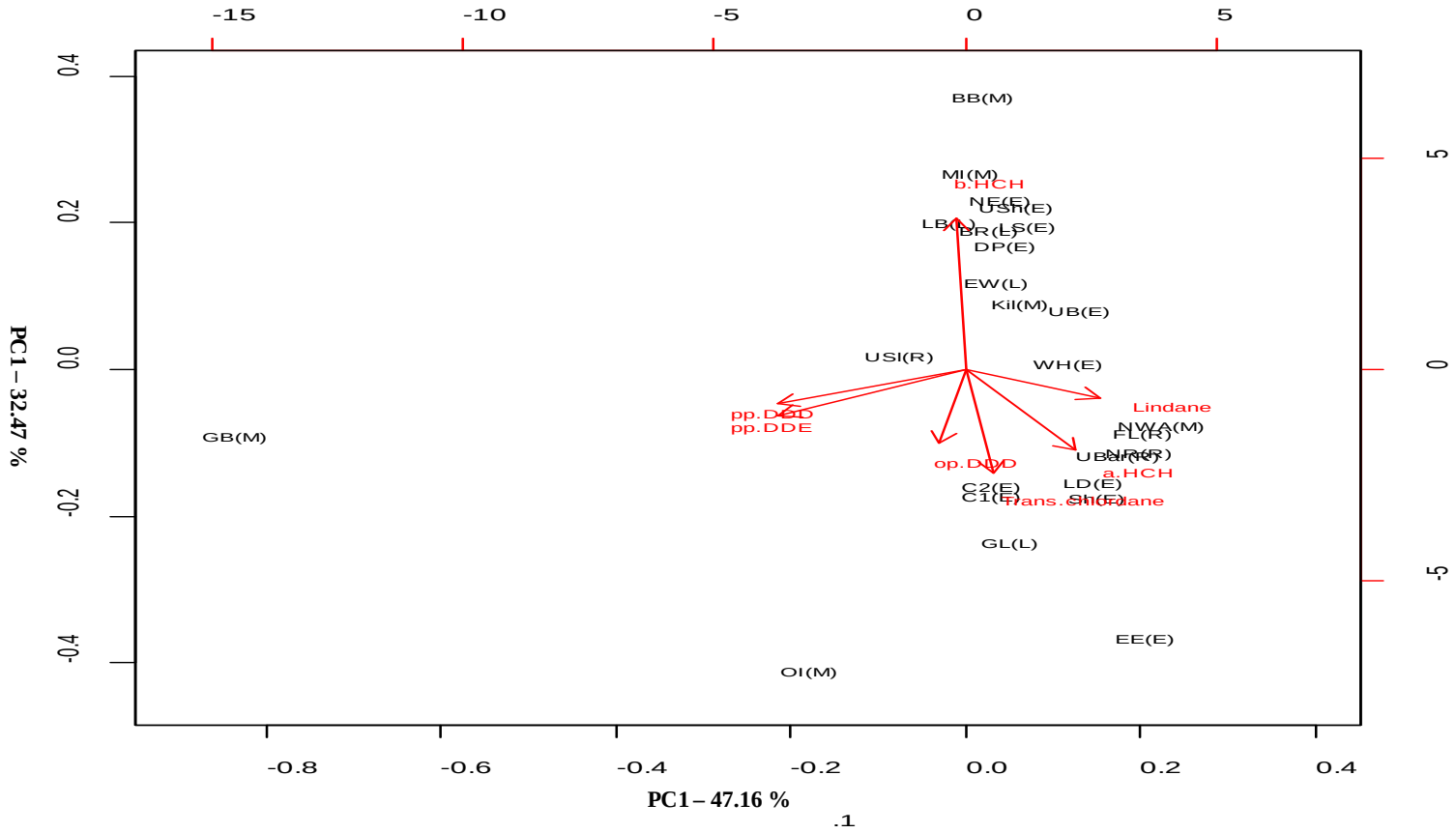


Figure 6.6: PCA plot (PC1 vs PC2) of concentration independent OC profiles for all sites. Letters in parenthesis indicate WB designation/type; M =Marine, E = Estuary, L= Lake and R = Riverine

evaluate site specific profiles in the presence of information on the overall levels in addition to the concentration independent plots. It is evident for the Gwebarra and Omey Island sites (GB(M) and OM(M) respectively) that they are spatially separated from other locations. This is primarily a function of low overall pollutant levels coupled with relatively low level occurrence of both *pp*-DDE and *pp*-DDD in the case of the Gweebarra site and due to the low level occurrence of a-HCH at Omey Island. While spatially separated the levels of all pollutants measured are low at these two sites ($\sum OC_7$ <1 ng/L). The cork samplers are once again in good agreement with each other and are influenced by increased levels of *pp*-DDD, *op*-DDD and *pp*-DDE as well as higher concentrations of *trans*-chlordane at the site.

6.2.4 Assessment of BFR C_w Concentrations from Irish Waters

Until relatively recently reliable *Log* K_{pw} values were unavailable for PBDE congeners thus analysis and quantification of dissolved PBDE levels in PDMS samplers is a recent development. Analysis of PDBE compounds in PDMS PSD was completed for a suite of six PBDEs (28, 47, 99, 100, 154 and 183) at 12 sites with full data sets available for statistical evaluation at 11 of these (exception Upper Barrow interference for PBDE 154). As per PCBs it was possible to report PBDE concentrations in pg/L, a task which is currently difficult to achieve with conventional spot sampling techniques.

Upperbound $\sum BFR_6$ C_w concentrations ranged from 4.34 pg/L at the North Western Atlantic site to 85.4 pg/L in the Nore estuary site. There are few literature publications

currently available in relation to levels of PBDEs in deployed PDMS passive samplers apart from that of the NORMAN [194] network study and then only from one wastewater treatment plant site (33.2 pg/L) which is on a similar scale to this study. As such, direct comparisons to literature values are not yet possible. Major percentage contributions to the total ∑6BFRs from the PSDs were noted from PBDE 47 (up to 57.9%) with significant contributions also evident for PBDE 99.

Lowest levels were evident at the three coastal sites on the West of Ireland (Gweebarra, NWA and Kilkieran) all of which exhibited dissolved concentrations of PBDEs at less than 10 pg/L for ∑6BFRs. PCA plots below (*Figure 6.7* and *6.8*) show that in general the estuarine and river sites are found together while the marine sites are separate (apart from Lough Furnace – (LF(R))).

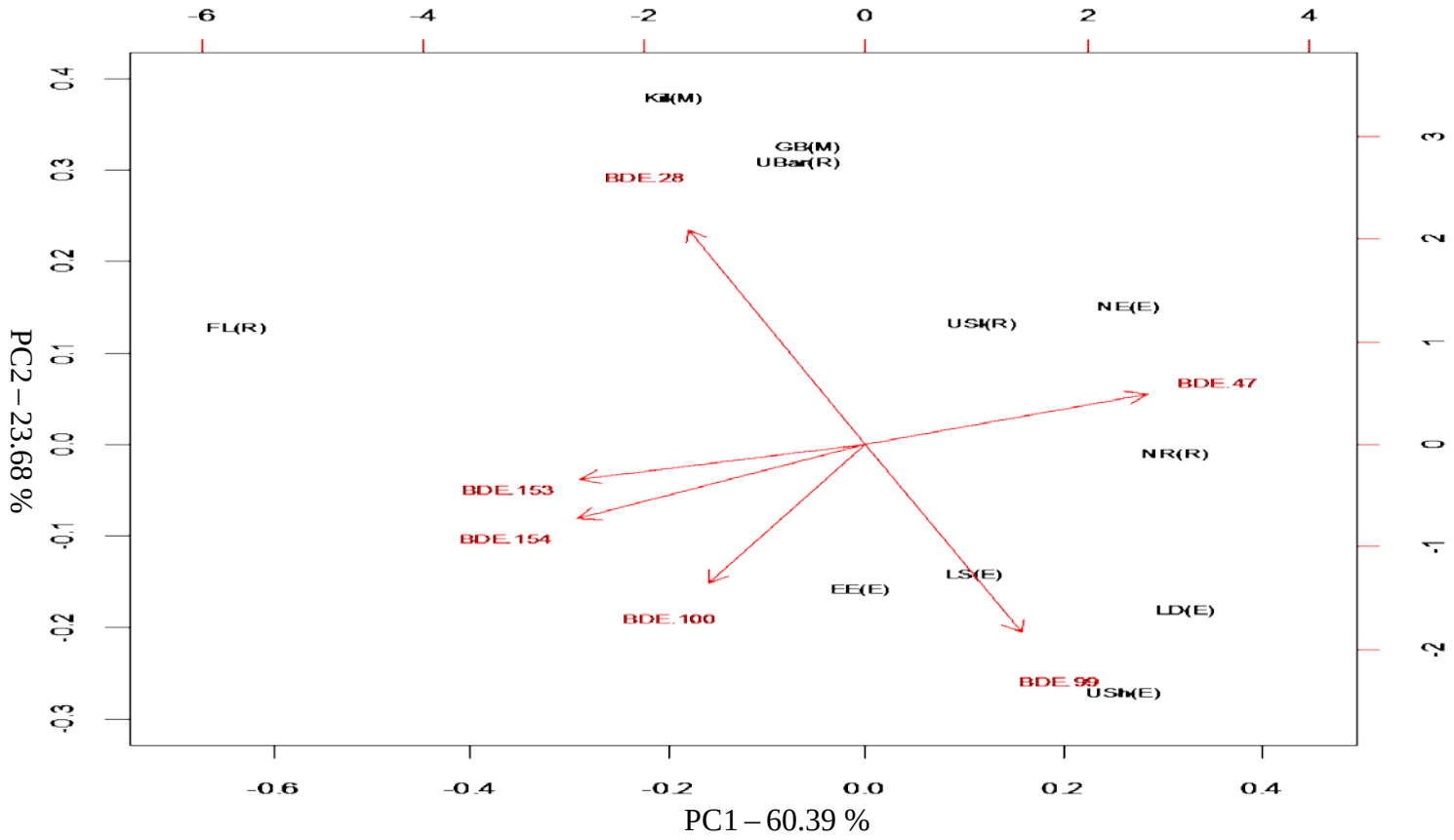


Figure 6.7: PCA plot (PC1 vs PC2) of concentration independent PBDE profiles for all sites. Letters in parenthesis indicate WB designation/type; M =Marine, E = Estuary, L= Lake and R = Riverine.

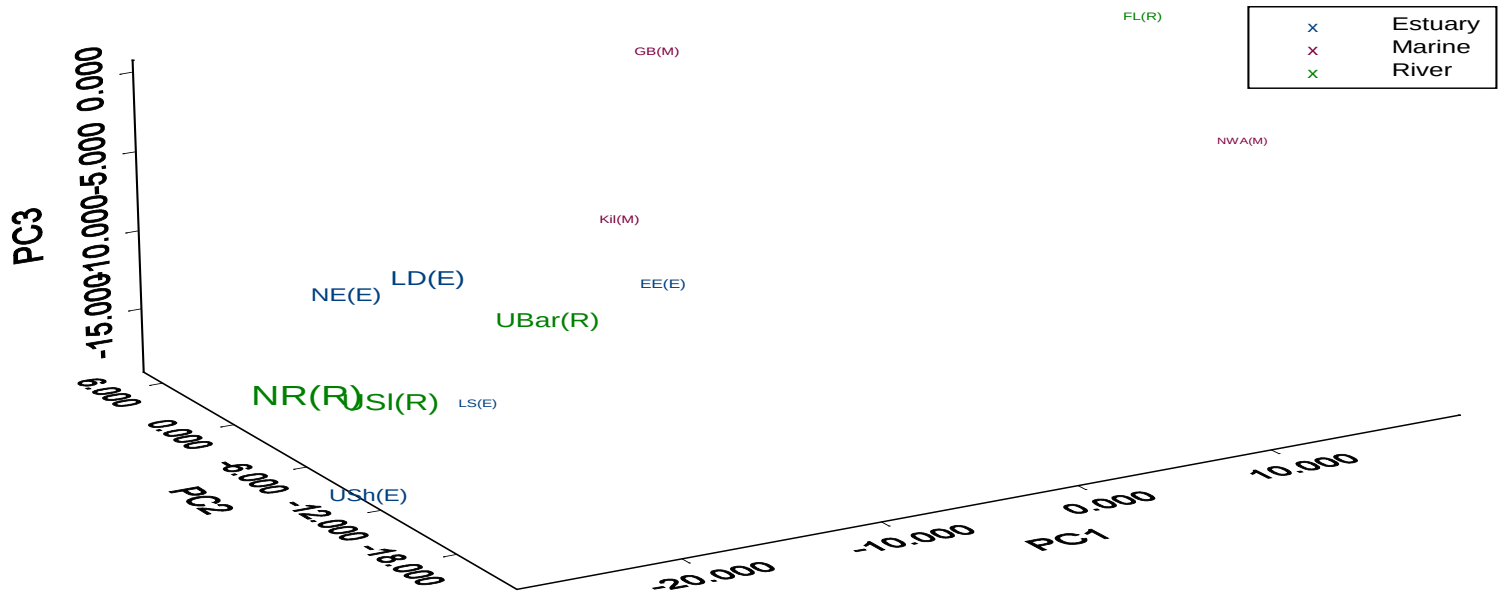


Figure 6.8: 3D PCA plot (PC1 vs PC2 Vs PC3) of concentration independent PBDE profiles (based on sum 6 PBDEs) for all sites and WB designation/types. Symbol size dictates concentration of $\sum PBDE_6$ (PC1 – 60.39 %, PC2 – 33.68 and PC3 – 15.92 %).

6.3 Conclusions

It has been demonstrated that passive samplers are easy to prepare, spike and deploy but also easy to extract and analyse instrumentally. They show many advantages over traditional sampling methods resulting in a more environmentally relevant dissolved water concentration which can take into account temporal and spatial trends over the deployment period. The deployment system itself was found to be robust with few losses of membranes or sampler cages encountered.

The PSDs have been found to be easy to extract and the resulting sample has been generally found to be free of many of the instrumental interferences often encountered when extracting other marine matrices including sediment and biota. Given the "multiplication" factor as a result of uptake over an extended time period, instrumental sensitivity issues associated with direct extraction and measurement of water are also addressed using PSDs.

This relatively large scale applied study documents the deployment and quality assured analysis of a variety of hydrophobic pollutants in a range of waterbody types. The importance of the rigid application of correct procedures (*e.g.* evaluation of the influence of salting out effects) for pollutant modelling has been demonstrated. The applied demonstration of the influence of this effect shows that such fundamental knowledge is key to the accuracy of measurement of pollutant levels.

In general dissolved hydrophobic pollutant burdens are relatively low in all Irish waters with those in the West and Southwest of Ireland found to be lower than those at other locations around Ireland. The application of a combination of concentration dependent

and concentration independent PCA profiling techniques has proven to be a valuable technique in indentifying site specific potential influences.

A number of locations on the West coast of Ireland have been identified as being potentially suitable for the purposes of classification as “reference/baseline” sites for a range of pollutants. Further to this valuable data (incorporating salting out effects correction) are reported for a range of pollutants adding to the low number of such datasets available in the literature. Such data are valuable in the marine sphere and specifically for the purposes of future proposals in respect of the generation of marine based assessment criteria for passive samplers, where currently few such datasets exist.

Chapter 7: Integration of PS Results with Legislative Requirements Including the WFD

7.1 Introduction

The use of passive samplers as part of a 'toolbox' of techniques to monitor the marine environment and to ultimately satisfy WFD and other legislative requirements is dependent on the technique overcoming various parameters as set out in the relevant legislation. The WFD for example has a number of requirements expected from monitoring to which the PSDs must show adherence (discussed in chapter 2) however the WFD does not state what method can be used to fulfil the requirements hence passive sampling could represent a next best method where increased sensitivity is required.

Technical and applied aspects of passive sampling have been thoroughly evaluated throughout this study specifically in respect of analytical challenges and of the technical performance of PSDs in a variety of locations encompassing varied saline conditions, hydrodynamic environments and deployment periods. Making use of the information gained throughout this study the three primary aims of this final chapter, namely;

1) Assessment of the data collected from all of the deployments throughout this study in relation to available assessment criteria;
2) Generation of a pilot "IRef" (Irish Reference concentration) from data collected from remote/pristine Irish sites and further comparison of this value to current OSPAR BACs;
3) Discussion of legislative aspects and particularly the application of passive sampling in support of the WFD.

Ultimately this chapter seeks to compare collected data to relevant criteria and use the information generated to give an indication of the overall 'status' of Irish waters relative to other locations. Further to this information collected in all chapters will then provide the focus for the generation of conclusions and recommendations on the wider applicability (and areas of ongoing research) with respect to a role for passive sampling in future environmental monitoring programs.

7.1.1 Assessment Criteria for PS

Even in the presence of the growing volumes of validation/support information, dissolved water concentrations (C_w) as calculated using passive samplers are not currently accepted as direct substitutes for traditional water sampling data and currently most assessment criteria have been generated based on the total water concept. WFD EQS values (for example) are not readily applicable to dissolved C_w values (as calculated using passive samplers) because they include levels of contaminants accumulated by and measured in particulate matter *e.g.* SPM, DOC *etc*.

As previously discussed the PSD derives truly dissolved values of contaminants hence in order to be "accepted" passive samplers will either require their own freely dissolved water concentration EQS values or, as has been documented, conversions can be achieved by taking the total water EQS value and converting it to a freely dissolved EQS by assuming a 30 mg/L suspended matter and 10 % organic carbon.[135]

Within the OSPAR convention process (primarily via the Marine Chemistry Working Group, MCWG) initial steps are in progress to enable the development of background

concentrations (BC) and background assessment concentrations (BAC) from available data (pg/L) from passive sampling and other means from “remote/pristine” areas.

The following sections of this chapter document the derivation of and direct application of assessment criteria from both the WFD and OSPAR-MCWG, as those currently most relevant, to attempt to elucidate the state of the Irish marine environment with respect to both of these criteria. Further to this, this chapter proposes a “pilot” Irish Reference concentration generated in a similar means to that of the OSPAR-MCWG values and discusses these in the context of the currently proposed BACs.

7.1.2 WFD Assessment Criteria

The WFD EU directive (2000/60/EC) was published and entered into force in December 2000 to provide a legislative framework to protect and improve the quality of waters.[11] A key element of WFD implementation is the establishment of River Basin Districts, and the island of Ireland has been divided into eight such districts, each comprising groups of adjoining river basins or catchments.[195] The WFD requires that the status of each of the river basins is determined through the assessment of various criteria such as ecological or chemical status. Of greater interest to this study was the chemical status. WFD classification systems and environmental quality standards (EQS) were developed for priority substances or groups of substances. Annex X of the WFD lists 33 priority pollutants for consideration as well as 8 further pollutants (or groups of pollutant) which fall outside of the scope of the WFD but are classed as priority substances of interest (list is available in Appendix A.10 along with details of the applicability of PSDs).

As previously discussed where uptake of a contaminant is likely within a passive sampler, it may be possible to then convert this dissolved pollutant information into an

equivalent total water EQS equivalent. Appendix A.10 Table.1 details relevant compounds along with their potential for accumulation (and thus potential for modelling of dissolved levels) in passive samplers, the associated EQS values and where applicable their EQS-C_w values as calculated by Smedes *et al.* [14] The PSD EQS-C_w values (where available) are calculated using *Eqn. 7.1*:

$$EQS\ C_w = \frac{EQS\ Total\ Water}{1+[SM]f_{oc}\ K_{oc}} \qquad \text{Eqn 7.1}$$

Where the EQS Total Water value is that specified by the WFD, SM is the suspended matter (30 mg/L), f_{oc} is the organic carbon content (0.1) and K_{oc} is the organic carbon water partition coefficient. It should be noted that the values used for normalisation purposes (suspended matter - 30 mg/L and f_{oc} is the organic carbon content - 0.1) suggested by Smedes are at the upper range of values expected in Irish waters and thus normalisation to these "constants" provides a strong basis for the "worst-case" scenario in terms of modelling dissolved water concentrations.

The generated criteria were then applied to the majority of data from all passive sampler deployments associated with this study. *Tables 7.1*, *7.2* and *7.3* illustrate how the EQS values were used to determine the status of a site in relation to the levels of relevant POPs present.

For the purposes of this assessment where concentration values were deemed not to be present *i.e.* n.d or as less than values they were removed from this current pilot assessment. A grey shaded value indicates that the C_w concentration for the site is below

the EQS-C_w, a blue shaded value indicates that the value reported is above the EQS-C_w concentration but below the actual EQS and a green shaded value means that a value is above the EQS. For this assessment absolute analytical data were directly compared to the relevant assessment criteria. Colour classifications followed the order of;

Below EQS-*Cw*	**Above EQS-*Cw***	**Above EQS**

Table 7.1 PSD C_w concentration values (ng/L) for the Burrishoole and M6 deployments and associated WFD EQS and EQS-C_w values. Shaded areas indicate the concentration with respect to the EQS.

Below EQS-Cw															WFD	WFD	
Above EQS-C_w															EQS	EQS	
Above EQS		Eel	Lough	Gallaghers	M6 250 M		M6 750 M		M6 1040 M		M6 PDMS PSD				Inland	Other	EQS-Cw
Compound ng/L	Black River	Wier	Bunevella	Lake	SPMD 1	SPMD 2	SPMD 1	SPMD 2	SPMD 1	SPMD 2	5M	250M	750M	1040M	(ng/L)	(ng/L)	(ng/L)
Anthracene	0.31	0.80	0.19	0.31	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.01	100	100	90
Fluoranthene	3.06	15.60	9.60	3.72	0.02	0.02	0.09	0.09	0.07	0.08	0.04	0.04	0.10	0.08	100	100	70
Benzo(b)fluoranthene	0.14	3.28	1.65	0.29	0.01	0.01	0.01	0.01	0.01	0.01	0.003	0.004	0.004	0.001	15	15	5
Benzo(k)fluoranthene	0.13	2.16	1.16	0.26	0.004	0.003	0.004	0.003	0.004	0.005	0.002	0.003	0.003	0.001	15	15	2
Benzo(a)pyrene	0.06	0.49	0.35	0.16	0.0007	0.001	0.001	0.001	0.001	0.001	0.01	0.002	0.0001	0.001	50	50	17
Indeno(1,2,3-cd)pyrene	0.09	0.89	0.48	0.22	0.0003	0.0001	0.0003	0.0001	0.0004	0.0008	0.001	0.0002	0.00002	0.0001	1	1	0.2
Benzo(g,h,i)perylene	0.06	0.58	0.35	0.23	0.0003		0.0003	0.0002		0.0003	0.0005	0.0003	0.0002	0.0001	1	1	0.11
α-HCH	3.32	2.91	2.36	0.66	0.03	0.03	0.05	0.06	0.04	0.03	0.14	0.10	0.09	0.07			
β-HCH	3.4	2.09	3.11								0.27	0.27	0.17	0.15			
γ-HCH	2.64	1.34	1.17	1.22	0.03	0.04	0.02	0.01	0.03	0.07							
∑HCH	9.36	6.34	6.64	1.88	0.07	0.07	0.07	0.07	0.07	0.11	0.41	0.37	0.26	0.22	20	2	2
op-DDD	0.004					0.0001	0.0001	0.0008	0.0007	0.0004	0.0004						
op-DDT	0.23	1.12	0.65	0.54		0.001	0.002	0.004	0.005	0.004	0.004		0.0004	0.0001			
pp-DDE	0.06	0.24	0.3	0.27	0.001	0.001	0.004	0.005	0.003	0.004	0.0001	0.0002	0.0003	0.0002			
op-DDE					0.002	0.002	0.007	0.009	0.006	0.008	0.002	0.001	0.001	0.002			
pp-DDD					0.0004	0.0004	0.003	0.003	0.001	0.001	0.005	0.003	0.001	0.001			
pp-DDT	0.2	0.94	0.31	0.1	0.0003	0.001	0.004	0.005	0.004	0.003	0.001	0.0003	0.0001	0.000			
∑DDT	0.49	2.30	1.26	0.91	0.005	0.006	0.02	0.03	0.02	0.02	0.008	0.004	0.003	0.004	25	25	25
HCB	0.03	0.05	0.03	0.01	0.01	0.01	0.02	0.02	0.01	0.02	0.0001	0.0003	0.0003	0.001	100	100	10
Endosulfan					0.03	0.03	0.03	0.04	0.03	0.03					5	0.5	0.5

Table 7.2 PSD C_w concentration values (ng/L) for the WFD sampled sites with associated WFD EQS and EQS-C_w values Shaded areas indicate the concentration with respect to the EQS.

Below EQS-Cw																
Above EQS-C_w														WFD	WFD	
Above EQS														EQS	EQS	
	NWA	Gweebarra	Erne	Furnace		Lower	Upper	Limerick	upper	New	upper	Nore	upper	Inland	Other	EQS-Cw
Compound ng/L	Seaboard	Bay	Estuary	Lough	Kilkeiran	Shannon	Shannon	Dock	Blackwater	Ross	Barrow	Estuary	Slaney	(ng/L)	(ng/L)	(ng/L)
Anthracene	1.02	0.60	5.75	0.11	0.23	1.20	1.08	0.41	0.49	3.56	1.90	3.43	4.35	100	100	90
Fluoranthene	0.50	0.65	5.76	1.24	1.87	2.65	3.01	6.25	4.30	4.93	6.45	4.64	3.67	100	100	70
Benzo(b)fluoranthene	0.01	0.01	0.07	0.02	0.01	0.03	0.07	0.12	0.03	0.22	0.05	0.03	0.01	15	15	5
Benzo(k)fluoranthene	0.004	0.01	0.11	0.04	0.02	0.05	0.11	0.19	0.04	0.29	0.08	0.10	0.01	15	15	2
Benzo(a)pyrene	0.003	0.01	0.06	0.04	0.01	0.03	0.06	0.14	0.02	0.18	0.03	0.04	0.01	50	50	17
Indeno(1,2,3-cd)pyrene	0.003	0.003	0.06	0.02	0.01	0.01	0.03	0.07	0.02	0.11	0.04	0.03	0.07	1	1	0.2
Benzo(g,h,i)perylene	0.002	0.002	0.09	0.02	0.01	0.02	0.04	0.09	0.03	0.13	0.03	0.02	0.10	1	1	0.11
α-HCH	2.38		5.02	4.02	0.13	2.6	4.18	7.62	2.04	1.83	6.74	3.62	1.74			
β-HCH					0.07	3.05	4.68	0.56	1.12			4.12	0.99			
γ-HCH	2.61	0.03	3.99	3.47	0.04	2.94	3.66	4.7	3.01	2.74	4.34	2.58	0.78			
∑HCH	4.99	0.03	9.01	7.49	0.24	8.59	12.52	12.88	6.17	4.57	11.08	10.32	3.51	20	2	2
op-DDD	0.0003	0.0001	0.01	0.001	0.001	0.03	0.01	0.2	0.01	0.02	0.03	0.02	0.06			
pp-DDD	0.0003		0.05	0.001	0.004	0.03	0.18	0.06	0.08	0.05	0.21	0.11	0.36			
pp-DDE	0.001	0.2	0.04	0.001	0.001	0.04	0.09	0.15	0.03	0.02	0.13	0.09	0.27			
op-DDE	0.0004	0.0002	0.003	0.0003	0.0009	0.01	0.02	0.06	0.001	0.0004	0.002	0.0003	0.002			
∑DDT	0.002	0.20	0.10	0.00	0.01	0.11	0.30	0.47	0.12	0.09	0.37	0.22	0.69	25	25	25
BDE 28	0.0001	0.002	0.0008	0.0021	0.002	0.0008		0.003	0.002	0.003	0.006	0.008	0.007	0.08	0.03	0.01
BDE 47	0.0008	0.003	0.007	0.0013	0.0043	0.007	0.022	0.031	0.024	0.039	0.026	0.046	0.047	0.08	0.03	0.002
BDE 100		0.001	0.0020		0.001	0.002	0.006	0.006	0.003	0.007	0.006	0.007	0.010	0.08	0.03	0.0002
BDE 99	0.001	0.002	0.003	0.0008	0.001	0.002	0.008	0.021		0.015	0.003	0.019	0.011	0.08	0.03	0.0002
BDE 154	0.0007				0.001	0.0005			0.004	0.001	0.002	0.002	0.004	0.08	0.03	0.00003
BDE 153										0.002	0.008	0.003		0.08	0.03	0.00003
∑PBDE	0.003	0.008	0.01	0.004	0.009	0.01	0.04	0.06	0.03	0.07	0.04	0.08	0.08	0.5	0.2	0.01

Table 7.3 PSD C_w concentration values (ng/L) for the non-WFD industrial sites with associated WFD EQS and EQS-C_w values. Shaded areas indicate the concentration with respect to the EQS.

Below EQS-Cw											
Above EQS-C_w									WFD	WFD	
Above EQS									EQS	EQS	
	Mutton	Dublin	Bantry	Omey			Wexford		Inland	Other	EQS-Cw
Compound ng/L	Island	Port	Bay	Island	Cork 1	Cork 2	Harbour	Shannon	(ng/L)	(ng/L)	(ng/L)
Anthracene	0.16	0.89	0.16	0.05	0.48	0.63	1.26	0.70	100	100	90
Fluoranthene	1.02	5.47	0.66	0.52	5.60	4.98	5.45	5.97	100	100	70
Benzo(b)fluoranthene	0.04	0.89	0.02	0.02	0.76	0.67	0.88	0.11	15	15	5
Benzo(k)fluoranthene	0.03	0.54	0.02	0.02	0.76	0.64	0.77	0.11	15	15	2
Benzo(a)pyrene	0.02	0.67	0.005	0.01	0.28	0.22	0.19	0.04	50	50	17
Indeno(1,2,3-cd)pyrene	0.01	0.19	0.01	0.01	0.47	0.31	0.18	0.03	1	1	0.2
Benzo(g,h,i)perylene	0.01	0.24	0.003	0.004	0.39	0.27	0.14	0.03	1	1	0.11
α-HCH	1.77	1.74	0.73	0.51	5.52	5.39	4.87	8.12			
β-HCH	2.84	7.13	3.43	0.004	3.73	3.47	2.1				
γ-HCH	1.35	10.4	2.22	0.09	6.17	6.09	6.09	6.12			
∑HCH	5.96	19.27	6.38	0.604	15.42	14.95	13.06	14.24	20	2	2
op-DDD	0.05	0.45	0.03	0.04	0.49	0.45	0.04	0.15			
op-DDT	0.05	0.49	0.08	0.45							
pp-DDD	0.003	0.11	0.02	0.11	0.91	0.92	0.46	0.5			
pp-DDE	0.09	0.34	0.003	0.12	0.36	0.41	0.08	0.05			
pp-DDT	0.0003	0.06	0.01	0.04	1.47	1.58	0.13	0.33			
∑DDT	0.1933	1.45	0.143	0.76	3.23	2.91	0.67	0.88	25	25	25
HCB	0.12		0.03		0.20	0.20	0.06	0.12	100	100	10

The data shown in *Table 7.1* indicates that the data generated for the Burrishoole and M6 deployments compares well with the EQS (and calculated dissolved EQS-C_w) values. The grey shading for the majority of POPs in both sites indicates that, particularly at M6, the concentrations of contaminants are below the EQS-C_w values suggested by Smedes *et al.* [14] and far below the actual WFD EQS values. The PSD derived C_w values for the M6 are at levels very close to zero which would be as expected in such a remote area. The C_w concentrations in the Burrishoole samplers are also at low levels compared to EQS values.

Official WFD sites (*Table 7.2*) sampled as part of this study also seem to have levels which are low overall. For PAHs all C_w concentrations are low (below EQS-C_w) apart from slightly elevated benzo(g,h,i)perlyene from the New Ross sampler however they are still below the WFD EQS concentrations. ∑HCHs are raised relative to criteria at a number of locations but are still below the EQS values. BFRs on the other hand are mostly above the modelled EQS-C_w concentrations but well below the WFD-EQS values. It must be noted that the concentrations of PBDEs as mandated within the WFD are generally considered to be extremely low and consequently passive samplers are generally deemed to be one of the few practical techniques applicable to monitor for these compounds close to the mandated limit.

Table 7.3 indicates that PAHs are again generally well below the WFD EQS with only 4 locations (which are more industrial in nature) showing levels higher than the EQS-C_w values for indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene. ∑HCHs are once again raised (with the exception of the remote Omey Island site) with the Dublin site close to exceeding the actual WFD-EQS value. In a general context

levels in the Irish sites reported are below the EQS values set out in the WFD with some sites having concentrations just above the EQS-C_w.

7.1.3 MCWG Assessment Criteria

The marine chemistry working group (MCWG) primarily concentrates its work around the status and fate of environmental pollutants (organics and metals) as well as emerging substances of concern with subsequent advice tendered to ICES. In March 2013 the MCWG reported findings as related to passive sampling. These findings were primarily derived via the preparatory work of a number of OSPAR and ICES working groups and compiled via the Steering Group on Human Interactions on Ecosystems (SCICOM).

The overall findings suggest that there was a need for a framework for further interpretation and evaluation of passive sampling data. Preliminary freely dissolved background assessment criteria (BAC) and background concentrations (BC) for PAHs and PCBs and OCs were generated for use in OSPARs CEMP assessment of temporal trends with the ultimate aim of achieving concentrations in the marine environment at near background levels and at close to zero for manmade synthetic substances. [196]

BAC and BC assessment criteria were created using datasets from remote ‘pristine’ areas from across Europe observed in different studies which included passive samplers and direct water measurement. Via a process of determining the lower quartile allied to the background concentration (BC) for the relevant pollutant a BAC

was generated. It must be noted that currently a number of reservations and restrictions have been placed on the application of these values, primarily that that they are not currently deemed sufficiently robust for wider application in the CEMP assessment process.

For the purposes of this smaller scale assessment these values were then used to assess the data generated by passive samplers throughout this study in a similar manner to that performed using WFD EQS as shown in *Tables 7.1, 7.2* and *7.3*. A grey shaded area indicates a value less than the proposed BC, a blue shaded value is one that is higher than the BC but below the BAC and a green shaded value is above the BAC. Once again any less than or not detected values are removed.

Below BC	**Above BC <BAC**	**>BAC**

Further to this the generation of a pilot Irish Reference concentration (IRef) based on the methodology applied for the generation of the initial BAC will be discussed.

Table 7.4: PSD C_w concentration values (ng/L) from a range of Irish locations (including industrialised and "pristine" sites) in addition to the Burrishoole catchment assessed using the BAC. Shaded areas indicate the concentration with respect to the BC and BAC

Below BC		Above BC		Above BAC										
	Mutton	Dublin	Bantry	Omey			Wexford		Black	Eel	Lough	Gallaghers		
Location (ng/L)	Island	Port	Bay	Island	Cork 1	Cork 2	Harbour	Shannon	River	Wier	Bunevella	Lake	BC ng/L	BAC ng/L
Phenanthrene	2.08	4.85	2.88	1.27	9.48	8.67	4.67	12.44	10.2	16.6	14.1	13	0.043	0.286
Anthracene	0.16	0.89	0.16	0.054	0.48	0.63	1.26	0.70	0.31	0.80	0.19	0.31	0.006	0.073
Fluoranthene	1.02	5.47	0.66	0.52	5.60	4.98	5.45	5.97	3.06	15.60	9.60	3.72	0.016	0.055
Pyrene	0.56	6.10	0.26	0.10	3.39	3.07	3.32	3.43	1.71	8.84	6.05	2.56	0.009	0.046
Chrysene	0.06	1.09	0.012	0.02	0.47	0.41	0.75	0.19	0.14	1.23	1.12	0.30	0.004	0.013
Benzo(a)anthracene	0.12	1.64	0.05	0.04	1.17	1.06	1.43	0.57	0.38	4.86	3.23	0.92	0.002	0.010
Benzo(b)fluoranthene	0.04	0.89	0.02	0.02	0.76	0.67	0.88	0.11	0.14	3.28	1.65	0.29	0.005	0.013
Benzo(k)fluoranthene	0.03	0.54	0.02	0.02	0.76	0.64	0.77	0.11	0.13	2.16	1.16	0.26	0.005	0.013
Benzo(a)pyrene	0.02	0.67	0.005	0.01	0.28	0.22	0.19	0.04	0.06	0.49	0.35	0.16	0.002	0.010
Indeno(1,2,3-cd)pyrene	0.013	0.19	0.01	0.01	0.47	0.31	0.18	0.03	0.09	0.89	0.48	0.22	0.001	0.009
Dibenzo(a,h)anthracene	0.006	0.07	0.001	0.003	0.11	0.05	0.04	0.003	0.06	0.30	0.16	0.13	0.0002	0.008
Benzo(g,h,i)perylene	0.011	0.24	0.003	0.004	0.39	0.27	0.14	0.03	0.06	0.58	0.35	0.23	0.001	0.009
α-HCH	1.77	1.74	0.73	0.51	5.52	5.39	4.87	8.12	3.32	2.91	2.36	0.66	0	0.04
γ-HCH	1.35	10.4	2.22	0.09	6.17	6.09	6.09	6.12	2.64	1.34	1.17	1.22	0	0.04
pp-DDE	0.09	0.34	0.003	0.12	0.36	0.41	0.08	0.05	0.06	0.24	0.3	0.27	0	0.001
HCB	0.12		0.03		0.20	0.20	0.06	0.12	0.03	0.05	0.03	0.01	0	0.001
Dieldrin									0.06	0.1	0.36	0.7	0	0.002
PCB 52			0.004		0.17	0.17		0.03	0.02	0.10	0.24	0.29	0	0.001
PCB 101			0.004		0.13	0.12			0.10	0.29	0.32	0.46	0	0.001
PCB 118	0.03	0.22	0.01	0.08	0.15	0.12	0.03	0.02	0.08	0.31	0.32	0.47	0	0.001
PCB 153	0.05	0.26	0.017	0.15	0.14	0.15	0.03	0.04	0.11	0.54	0.47	0.61	0	0.001
PCB 138	0.03	0.14	0.01	0.11	0.15	0.14	0.03	0.04	0.06	0.45	0.41	0.57	0	0.001
PCB 180	0.01	0.23	0.01	0.02	0.12	0.12	0.03	0.02	0.04	0.15	0.10	0.29	0	0.001

Table 7.5: PSD C_w concentration values (ng/L) for official WFD passive sampling locations assessed using the MCWG BAC. Shaded areas indicate the concentration with respect to the BC and BAC

Below BC		Above BC		Above BAC											
	NWA	Gweebarra	Erne	Furnace		Lower	Upper	Limerick	upper	New	upper	Nore	upper		
Location (ng/L)	Seaboard	Bay	Estuary	Lough	Kilkeiran	Shannon	Shannon	Dock	Blackwater	Ross	Barrow	Estuary	Slaney	BC ng/L	BAC ng/L
Phenanthrene	2.13	4.01	17.2	3.03	5.66	6.22	7.44	10.8	16.2	16.0	16.9	19.2	6.6	0.04	0.29
anthracene	1.02	0.60	5.75	0.11	0.23	1.20	1.08	0.41	0.49	3.56	1.90	3.43	4.35	0.01	0.07
Fluoranthene	0.50	0.65	5.76	1.24	1.87	2.65	3.01	6.25	4.30	4.93	6.45	4.64	3.67	0.02	0.06
Pyrene	0.16	0.37	3.58	0.77	0.84	2.49	2.63	4.40	2.47	4.13	3.70	3.16	4.88	0.01	0.05
Chrysene	0.01	0.02	0.30	0.07	0.06	0.16	0.31	0.62	0.19	0.79	0.53	0.20	0.04	0.004	0.01
Benzo(a)anthracene	0.03	0.07	0.51	0.12	0.11	0.15	0.25	0.65	0.27	0.64	0.38	0.28	0.06	0.002	0.01
Benzo(b)fluoranthene	0.01	0.01	0.07	0.02	0.01	0.03	0.07	0.12	0.03	0.22	0.05	0.03	0.01	0.005	0.01
Benzo(k)fluoranthene	0.004	0.01	0.11	0.04	0.02	0.05	0.11	0.19	0.04	0.29	0.08	0.10	0.01	0.005	0.01
Benzo(a)pyrene	0.003	0.01	0.06	0.04	0.01	0.03	0.06	0.14	0.02	0.18	0.03	0.04	0.01	0.002	0.01
Indeno(1,2,3-cd)pyrene	0.003	0.003	0.06	0.02	0.01	0.01	0.03	0.07	0.02	0.11	0.04	0.03	0.07	0.001	0.01
Dibenzo(a,h)anthracene	0.0005	0.0005	0.01	0.003	0.0002	0.003	0.01	0.005	0.02	0.01	0.005	0.01	0.01	0.0002	0.01
Benzo(g,h,i)perylene	0.002	0.002	0.09	0.02	0.01	0.02	0.04	0.09	0.03	0.13	0.03	0.02	0.10	0.001	0.01
α-HCH	2.38		5.02	4.02	0.13	2.6	4.18	7.62	2.04	1.83	6.74	3.62	1.74	0	0.04
γ-HCH	2.61	0.03	3.99	3.47	0.04	2.94	3.66	4.7	3.01	2.74	4.34	2.58	0.78	0	0.04
pp-DDE	0.001	0.2	0.04	0.001	0.001	0.04	0.09	0.15	0.03	0.02	0.13	0.09	0.27	0	0.001
Dieldrin	0.002	0.0001	0.07	0.05	0.02	0.03	0.12	0.21	0.35	0.86	0.51	0.57	1.19	0	0.002
PCB 28	0.02	0.008	0.047	0.010	0.002	0.010	0.021	0.094	0.028	0.071	0.031	0.022	0.04	0	0.001
PCB 52	0.004	0.003	0.007	0.014	0.0009	0.007	0.027	0.072	0.017	0.051	0.007	0.011	0.02	0	0.001
PCB 101	0.005	0.008	0.011	0.004	0.0006	0.009	0.029	0.053	0.011	0.038	0.005	0.004	0.01	0	0.001
PCB 118	0.005	0.010	0.004	0.002	0.002	0.006	0.020	0.024	0.004	0.047	0.007	0.013	0.01	0	0.001
PCB 153	0.004	0.034	0.045	0.013	0.004	0.008	0.021	0.034	0.006	0.026	0.009	0.012	0.02	0	0.001
PCB 138	0.0013	0.013	0.007	0.004	0.001	0.007	0.015	0.017	0.003	0.013	0.003	0.005	0.004	0	0.001
PCB 180	0.003	0.002	0.004	0.004	0.0005	0.005	0.007	0.010	0.001	0.006	0.001	0.004	0.004	0	0.001

Table 7.6: PSD C_w concentration values (ng/L) for the M6 deployment assessed using the MCWG BAC. Shaded areas indicate the concentration with respect to the BC and BAC

Below BC		Above BC		Above BAC							
	M6 250 M		M6 750 M		M6 1040 M		M6 PDMS PSD					
Compound ng/L	SPMD 1	SPMD 2	SPMD 1	SPMD 2	SPMD 1	SPMD 2	5M	250M	750M	1040M	BC ng/L	BAC ng/L
Phenanthrene	0.18	0.18	0.17	0.16	0.13	0.14	0.41	0.31	0.33	0.21	0.043	0.286
Anthracene	0.011	0.012	0.012	0.011	0.010	0.011	0.010	0.017	0.019	0.011	0.006	0.073
Fluoranthene	0.02	0.02	0.09	0.09	0.07	0.08	0.04	0.04	0.10	0.08	0.016	0.055
Pyrene	0.006	0.005	0.015	0.014	0.012	0.015	0.014	0.006	0.011	0.009	0.009	0.046
Chrysene	0.002	0.002	0.003	0.003	0.002	0.002	0.002	0.001	0.001	0.0004	0.004	0.013
Benzo(a)anthracene	0.01	0.01	0.02	0.02	0.02	0.02	0.005	0.005	0.01	0.007	0.002	0.01
Benzo(b)fluoranthene	0.007	0.006	0.01	0.007	0.01	0.01	0.003	0.004	0.004	0.001	0.005	0.013
Benzo(k)fluoranthene	0.004	0.003	0.004	0.003	0.004	0.005	0.002	0.003	0.003	0.001	0.005	0.013
Benzo(a)pyrene	0.001	0.001	0.001	0.001	0.001	0.001	0.005	0.002	0.0001	0.001	0.002	0.01
Indeno(1,2,3-cd)pyrene	0.0003	0.0001	0.0003	0.0001	0.0004	0.001	0.001	0.0002	0.00002	0.0001	0.001	0.009
Dibenzo(a,h)anthracene							0.0001				0.0002	0.008
Benzo(g,h,i)perylene	0.0003		0.0003	0.0002		0.0003	0.0005	0.0003	0.0002	0.0001	0.001	0.009
α-HCH	0.03	0.03	0.05	0.06	0.04	0.03	0.14	0.10	0.09	0.07	0	0.04
γ-HCH	0.03	0.04	0.02	0.01	0.03	0.07					0	0.04
pp-DDE	0.001	0.001	0.004	0.005	0.003	0.004	0.0001	0.0002	0.0003	0.0002	0	0.001
HCB	0.01	0.01	0.02	0.02	0.01	0.02	0.0001	0.0003	0.0003	0.001	0	0.001
Dieldrin	0.005	0.005	0.03	0.08	0.05	0.03	0.002	0.001	0.002	0.001	0	0.002
PCB 28	0.0007	0.0006	0.0012	0.002	0.0007	0.001	0.0004	0.0004	0.0006	0.0003	0	0.001
PCB 52	0.001	0.00104	0.0016	0.0016	0.0009	0.0008	0.0002	0.0003	0.0009	0.0004	0	0.001
PCB 101	0.0003	0.0003	0.0005	0.0004	0.0004	0.0004	0.0002	0.0004	0.0004	0.0003	0	0.001
PCB 118	0.0006	0.0006	0.002	0.002	0.0006	0.0005	0.0002	0.0002	0.0002	0.0003	0	0.001
PCB 153	0.0009	0.0009	0.002	0.002	0.002	0.002	0.0002	0.0004	0.0003	0.0003	0	0.001
PCB 138	0.0004	0.0004	0.001	0.0012	0.0007	0.0006	0.0006	0.0004	0.0003	0.0002	0	0.001
PCB 180	0.0001	0.0001	0.0003	0.0004	0.0003	0.0003	0.0001	0.0001	0.00009	0.00007	0	0.001

The results assessed with the MCWG BAC and BC values indicate that many areas have levels above what the MCWG consider background levels. For PAHs, the relatively industrialised areas (*Table 7.4)* are mostly shaded in green indicating that levels reported are above the BAC. Only a few areas such as Mutton Island, Omey Island and Bantry Bay have concentrations shaded in blue (below BAC but above BC) for PAHs.

The C_w concentrations reported at the official WFD sites (*Table 7.5*) are again shaded mostly green indicating levels above the BAC for PAHs, some sites (Kilkeiran, NWA and Gweebarra) have lower concentrations present (thus more blue shading) indicating that levels at these locations are lower than the other sites sampled and are mostly at just above BC levels for PAHs. In this context these locations (in addition to Bantry Bay and Omey Island) have been further selected for inclusion in the generation of the pilot IRef discussed below. While the levels are relatively low the majority of sites in *Table 7.5* are shaded green for PCBs and OCs indicating that levels at these locations are above the currently used BAC.

The deployment at the remote M6 weather buoy (*Table 7.6*) exhibits mostly grey and blue shaded areas indicating that the C_w concentrations reported here (particularly PAHs) are at very low concentrations. For PCBs and OC the shading is mostly blue indicating that the levels are above the BC (which is set to zero) with relatively few data exceeding the BAC.

The BC and BAC levels proposed by the MCWG are generally low in comparison to the WFD EQS values. Future ongoing development of these values is merited and the proposed values are subject to ongoing change in the future.[196] The merits of the inclusion of this present dataset in this ongoing BAC process are further discussed below.

7.1.4 Generation of a Pilot Marine Irish Reference (IRef) Concentration

As discussed throughout this chapter, levels of pollutants as derived by passive samplers are generally low in Irish waters. Each of the individual chapters has identified specific locations where few pressures are evident and in turn these locations have been selected for generation of the IRef value for a range of pollutants using the same concepts as those utilised for the generation of levels of the OSPAR BACs as reported earlier.

Pollutant levels from a number of Irish locations on the west coast (namely the North Western Atlantic Seaboard (NWA), Gweebarra Bay (GB), outer Bantry Bay (BB), Omey Island (OI) and Kilkieran (Kil) in addition to selected values from the M6 weather deployment location were selected. Where replicate values were available for M6 deployments (SPMDs only) the minimum value of the replicates was selected. Both SPMD and PDMS data were considered from all depths sampled. While the inclusion of only one concentration value for the M6 was considered, given the range of depths sampled the inclusion of all depth data was deemed to be relevant in the context of the potential different water masses at these depths. Absolute analytical data (*i.e.* upperbound values) were collated from each of the sites and the lower quartile

calculated for each parameter (IREABS (1/4ile pg/l) and reported in *Table 7.7*. Following this the current OSPAR BC value was then added to the derived lower quartile value to enable the derivation of an IRef concentration value.

Table 7.7 Generation of a pilot IRef concentration from Irish passive sampling data and reference to current OSPAR BAC for PAHs (ng/L) and PCB, OC and PBDE (pg/L).

IREF parameter	BB(M)	OI(M)	NWA(M)	GB(M)	KI(M)	M6 250 Min(O)	M6 750 Min(O)	M6 1040 Min(O)	M6 PDMS5M(O)	M6 PDMS250M(O)	M6 PDMS750M(O)	M6 PDMS1040M(O)	MIN (pg/L)	IRE ABS (1/4ile) ng/l	IRE ABS (1/4ile) pg/l	**IRef (1/4ile pg/l + BC)**	OSPAR BC(1/4ile)	95CI	OSPAR BAC (pg/l)	IrefC vs OSPAR BAC (%)	**IRef (1/4ile pg/l + BC)***	IRef vs OSPAR BAC (%)*
Acenaphthylene	1.36	0.30	0.10	2.80	0.16	0.03	0.02	0.03	0.04	0.01	0.004	0.003	2.89									
Acenaphthene	0.57	0.14	0.03	0.52	0.05	0.02	0.01	0.01	0.04	0.01	0.004	0.004	3.54									
Fluorene	2.85	0.67	0.08	0.10	0.04	0.06	0.05	0.04	0.05	0.02	0.01	0.01	10.9									
Phenanthrene	2.88	1.27	2.13	4.01	5.66	0.18	0.16	0.13	0.41	0.31	0.33	0.21	133	0.20	202	245	43.0	244	286	85.5	1,528	534
Anthracene	0.16	0.05	1.02	0.60	0.23	0.01	0.01	0.01	0.01	0.02	0.02	0.01	9.6	0.01	10.9	16.9	6.00	67.0	73.0	23.2	83.5	114
Fluoranthene	0.66	0.52	0.50	0.65	1.87	0.02	0.09	0.07	0.04	0.04	0.10	0.08	22.7	0.06	59.2	75.2	16.0	39.0	55.0	137	521	947
Pyrene	0.26	0.10	0.16	0.37	0.84	0.01	0.01	0.01	0.01	0.01	0.01	0.01	5.30	0.01	10.3	19.3	9.00	37.0	46.0	41.9	124	270
Chrysene	0.01	0.02	0.01	0.02	0.06	0.002	0.003	0.002	0.002	0.001	0.001	0.0004	0.40	0.001	1.31	5.31	4.00	8.00	13.0	40.8	14.0	108
Benzo(a)anthracene	0.05	0.04	0.03	0.07	0.11	0.01	0.02	0.02	0.005	0.005	0.01	0.01	4.90	0.01	9.14	11.1	2.00	8.00	10.0	111	34.5	345
Benzo(b)fluoranthene	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.003	0.004	0.004	0.001	1.37	0.004	3.81	7.81	4.00	8.00	11.0	71.0	14.0	127
Benzo(k)fluoranthene	0.02	0.02	0.004	0.01	0.02	0.003	0.003	0.004	0.002	0.003	0.003	0.001	1.34	0.003	3.05	8.05	5.00	8.00	13.0	61.9	10.5	80.8
Benzo(a)pyrene	0.01	0.01	0.003	0.01	0.01	0.001	0.001	0.001	0.005	0.002	0.0001	0.001	0.06	0.001	0.58	2.58	2.00	8.00	10.0	25.8	5.50	55.0
Indeno(1,2,3-cd)pyrene	0.01	0.01	0.003	0.003	0.01	0.0001	0.0001	0.0004	0.0006	0.0002	0.00002	0.00008	0.02	0.0001	0.10	1.10	1.00	8.00	9.00	12.2	4.00	44.4
Dibenzo(a,h)anthracene	0.001	0.003	0.001	0.001	0.0002	0.00004	0.00004	0.00004	0.00008	0.00002	0.00002	0.00002	0.02	0.00004	0.04	0.24	0.20	8.00	8.00	2.94	0.48	5.94
Benzo(g,h,i)perylene	0.003	0.004	0.002	0.002	0.01	0.00001	0.0002	0.00001	0.0005	0.0003	0.0002	0.0001	0.01	0.000	0.15	1.15	1.00	8.00	9.00	12.7	3.00	33.3
PCB 18	n.a*	n.a*	9.01	17.5	1.59	n.a	n.a	n.a	0.39	0.34	0.89	0.49		0.44	0.44	0.44					1.28	
PCB 31	<0.1	<0.42	9.6	12.0	1.04	0.87	0.52	0.56	0.41	0.34	0.57	0.36		0.44	0.44	0.44					0.87	
PCB 28	<0.4	<1.8	21.5	8.00	1.68	0.62	1.19	0.65	0.41	0.38	0.56	0.28		0.45	0.45	0.45			1.00	44.8	1.33	133
PCB 52	3.97	<0.02	4.11	2.56	0.85	0.97	1.58	0.76	0.19	0.29	0.88	0.40		0.58	0.58	0.58			1.00	58.0	0.85	85.0
PCB 44	<0.06	<0.32	3.45	6.62	0.49	0.87	1.21	0.16	0.11	0.25	0.85	0.25		0.25	0.25	0.25					0.40	
PCB 101	<0.02	<0.02	5.41	7.92	0.63	0.29	0.40	0.36	0.16	0.38	0.38	0.25		0.31	0.31	0.31			1.00	30.8	0.51	51.3
PCB 149	<0.05	8.30	2.78	1.36	0.33	n.d	n.d	n.d	0.12	0.21	0.31	0.15		0.06	0.06	0.06					0.33	
PCB 118	13.3	84.7	5.07	10.2	2.03	0.59	1.52	0.54	0.24	0.16	0.16	0.26		0.26	0.26	0.26			1.00	25.5	2.79	279
PCB 153	17.1	148	3.78	33.6	4.46	0.91	1.89	1.79	0.22	0.44	0.27	0.29		0.40	0.40	0.40			1.00	40.3	3.95	395
PCB 105	1.28	146	n.d	n.d	n.d	0.25	0.74	0.07	0.34	0.75	0.80	0.28		0.28	0.28	0.28					0.68	
PCB 138	10.6	113	1.28	13.1	1.20	0.42	1.06	0.55	0.56	0.42	0.25	0.15		0.42	0.42	0.42			1.00	42.0	1.22	122
PCB 156	<0.11	12.6	1.44	3.00	0.20	0.12	0.23	0.04	0.02	0.09	0.30	0.05		0.07	0.07	0.07					0.20	
PCB 180	5.45	23.7	3.39	1.55	0.51	0.14	0.34	0.28	0.11	0.10	0.09	0.07		0.11	0.11	0.11			1.00	10.8	0.77	77.0
PCB 170	3.23	2.98	0.33	0.20	<0.06	0.06	0.13	0.07	0.03	0.07	0.01	0.02		0.05	0.05	0.05					0.20	
PCB 194	3.09	2.81	<0.16	1.49	<0.16	n.a	n.a	n.a	<0.03	0.13	0.02	0.02		0.05	0.05	0.05					1.12	
PCB 209	<0.21	<1.32	0.49	1.01	<0.22	n.a	n.a	n.a	0.00	0.24	0.15	0.09		0.11	0.11	0.11					0.25	0.00
α-HCH	0.73	0.51	2.38	<0.01	0.13	0.03	0.05	0.03	0.14	0.10	0.09	0.07		0.06	0.06	0.06		40.0	40.0	0.15	0.13	0.33
β-HCH	3.43	0.004	n.a*	<0.02	0.07	0.000	0.00	0.00	0.27	0.27	0.17	0.15		0.001	0.001	0.001					0.003	
Endosulphane	0.001	0.002	n.d	n.d	n.d	0.03	0.03	0.03	n.d.	n.d.	n.d.	n.d.		0.002	0.002	0.002					0.002	
γ-HCH (Lindane)	2.22	0.09	2.61	0.03	0.04	0.03	0.01	0.03	n.d.	n.d.	n.d.	n.d.		0.03	0.03	0.03		40.0	40.0	0.08	0.03	0.08
op-DDD	0.03	0.04	0.0003	0.0001	0.001	0.0001	0.0007	0.0004	n.d.	n.d.	n.d.	n.d.		0.0003	0.0003	0.0003					0.0002	
op-DDT	0.08	0.45	n.d	n.d	n.d	0.001	0.004	0.004	n.d.	n.d.	n.d.	n.d.		0.004	0.004	0.004					0.041	
pp-DDD	0.02	0.11	0.0003	<0.30	0.004	0.0004	0.003	0.001	0.01	0.00	0.00	0.00		0.001	0.001	0.001					0.0004	
pp-DDE	0.003	0.12	0.001	0.20	0.001	0.001	0.004	0.003	0.0001	0.0002	0.0003	0.0002		0.0003	0.0003	0.0003		1.0	1.0	0.03	0.001	0.1000
pp-DDT	0.01	0.04	n.d	n.d	n.d	0.002	0.007	0.01	0.00	0.00	0.00	0.00		0.002	0.002	0.002					0.005	
Trans-chlordane	0.01	0.02	0.001	0.0003	0.001	0.001	0.002	0.001	n.d.	n.d.	n.d.	n.d.		0.001	0.001	0.001					0.001	
op-DDE	n.d	n.d	0.0004	0.0002	0.001	0.0003	0.004	0.003	0.001	0.0003	0.0001	0.0002		0.0002	0.0002	0.0002					0.0002	
Cis-chlordane	n.d	n.d	0.002	n.d	0.004	0.001	0.005	0.002	0.0004	0.001	0.001	0.0002		0.0005	0.0005	0.0005					0.0011	
Dieldrin	n.d	n.d	0.002	0.0001	0.02	0.005	0.03	0.03	0.002	0.001	0.002	0.001		0.002	0.002	0.002		2.0	2.0	0.08	0.001	0.044
HCB	0.03	n.d	n.d	n.d	n.d	0.01	0.02	0.01	0.0001	0.0003	0.0003	0.0009		0.0003	0.0003	0.0003		1.0	1.0	0.03	0.0076	0.7605
BDE 28	n.a	n.a	0.09	2.04	2.17	n.a	n.a	n.a	n.a	n.a	n.a	n.a		1.07	1.07	1.1					0.07	
BDE 47	n.a	n.a	0.81	3.26	4.31	n.a	n.a	n.a	n.a	n.a	n.a	n.a		2.04	2.04	2.04					0.61	
BDE 100	n.a	n.a	<0.70	0.78	1.37	n.a	n.a	n.a	n.a	n.a	n.a	n.a		0.93	0.93	0.93					0.39	
BDE 99	n.a	n.a	1.10	1.96	0.74	n.a	n.a	n.a	n.a	n.a	n.a	n.a		0.92	0.92	0.92					0.56	
BDE 154	n.a	n.a	0.66	<0.59	0.80	n.a	n.a	n.a	n.a	n.a	n.a	n.a		0.70	0.70	0.70					0.33	
BDE 153	n.a	n.a	<0.98	<0.94	<0.99	n.a	n.a	n.a	n.a	n.a	n.a	n.a		0.94	0.94	0.94					0.94	

With the exception of fluoranthene (137%) and Chrysene (111%) all other calculated values (highlighted in green) were lower than the current provisional BAC for the parameter. It should be noted that the incorporation of a greater number of sites from M6 in the dataset may influence the final outcome of the pilot assessment however given the different dynamics and water mass influences inclusion of the majority of these important data was deemed appropriate. To further test the robustness of the pilot IRef only one single value (*i.e.* the minimum for each parameter) was included in the generation of a second IRef value. Where only one value for the M6 was included the generate IRef (shaded yellow) exceeded the current OSPAR BAC for the lower ring PAHs but was still lower for the higher ring PAHs and for OCs. With the exception of PCBs (28, 118, 138 and 153) the generated IRef was below the BAC regardless of the inclusion of fewer M6 sites.

7.1.5 Summary conclusions

Silicone rubber passive sampling devices have proven to be a robust monitoring tool capable of sequestering a range of contaminants and providing environmentally relevant dissolved water concentrations which can take into account seasonal changes and point source discharges. Of the samplers deployed very few were lost and in the case where this happens the buoy to which the sampler was attached was missing.

The samplers themselves have proven easy to prepare, spike and deploy. The subsequent retrieval and extraction/analysis steps have proven equally simple. Modelling of contaminant uptake by PSDs in the environment using PRCs and the NLS method proposed by Booij and Smedes [119] has proven to be easily understood and

therefore overall it can be concluded that once familiar with the passive sampling technique it can be easy to use with simple instruction.

Levels of contaminants in Irish waters are generally low (even within more industrial areas) but some values exceed the BAC as currently reported. The use of data from the M6 compares well with the BAC concentrations generated by the MCWG which indicates that this is a key 'pristine' site. A number of elements are clear from this exercise namely;

1) The current BAC process is very subjective to both the availability of and inclusion/exclusion of data and the definition of a "spatial" selection procedure,
2) Data are presented for a range of parameters some of which have very few examples in the literature *e.g.* PBDEs and some OCs,
3) Rural/unimpacted coastal sites are generally not suitable for use in the derivation of BACs, data should where possible be restricted to that obtained from (salting out corrected) offshore data,
4) The importance of M6 as a site for both the generation of an IRef and for future OSPAR BACs is clear.

Based on the information provided throughout this study it is clear that (particularly) PDMS passive samplers are a useful technology, fit for purpose (in determining dissolved pollutant levels), straight forward and easy to use and can be deployed in the marine environment to derive C_w concentrations. These C_w values can then be subjected to currently proposed conversion techniques and can be used to support legislative and monitoring requirements. Some further conclusions, recommendations and calls for future research are detailed in section 7.2

7.2 Conclusions, Recommendations and Future Vision for PSDs

Overall this thesis broadly supports most of the findings recent workshop on passive sampling and passive dosing (WKPSPD) [197] which recognised that the most mature use of PSDs presently is in the detection and analysis of hydrophobic contaminants. Uncertainty around sampling rates means that PS for polar compounds (although useful in investigative monitoring) is not currently suitable for compliance monitoring.

As previously mentioned silicone rubber passive sampling devices have proven to be a robust monitoring tool capable of sequestering contaminants from the environments and providing dissolved water concentrations which can take into account seasonal and spatial changes and incorporate the changes in concentration that occur during point source discharges. The samplers themselves have proven to be manageable within the majority of well equipped laboratories in regards to preparation and use as well as instrumental analysis.

Key aims and the subsequent conclusions and recommendations of this thesis are now summarily discussed with recommendations delivered below under a number of headings, namely:

1) Technical aspects: lessons learned and data generated,
2) Passive sampling and the legislative/assessment context,
3) Future research needs and approaches,
4) Recommendations and a future role for passive sampling.

7.2.1 Technical Aspects: Lessons Learned and Data Generated

On a technical note and as previously mentioned the samplers themselves have proven easy to prepare, spike and deploy. The subsequent retrieval and extraction/analysis steps have proven equally simple. This thesis documents the ideal size and PDMS thickness to enable good broad scale sampling of a wide range of POPs. This thesis further reports clean-up and spiking procedures and reports simple QA procedures to support analysis and documents the importance of application and completion of salting-out adjustments (where applicable) to modelled data. Lohmann *et al.* [147] further note the relative influence of temperature and other environmental factors on performance, however in general these are deemed to be relativly small in the context of overall uncertainties associated with such applications. This thesis demonstrates the application of PS devices in cold deep water high pressure environments in addition to near surface sampling as well as inshore and inland deployments. Modelling of contaminant uptake by PDMS PSDs in the environment was completed using PRCs and the NLS method proposed by Booij and Smedes [119] and has proven to be easily understood and therefore overall it can be concluded that once familiar with the passive sampling technique it can be easy to use with simple instruction.

Passive sampling as a relevant tool will be enhanced by future development of a proficiency testing scheme whereby laboratories can further develop their techniques and then use the derived analytical information (and PS materials) for wider QA purposes. Such a scheme could take a similar format to the PSTS survey of 2007 [118] where samplers were prepared at a reference laboratory, in line with current best practice, and the samplers distributed to participating laboratories for analysis with the results returned to the central laboratory. The data generated could give an insight into

the performance of all laboratories involved and an indication of the analytical variability of passive sampling and support the fitness for purpose of PS.

The current WFD QA/QC Directive requires a combined uncertainty of <50% at the EQS concentration. Whilst a 50% uncertainty target is generally achievable for the determination of analyte concentrations within the passive sampler itself, difficulties exist in doing so for passive sampling based C_w due to there being additional error sources (*e.g.* K_{pw} values of the analytes and PRCs). Because sampling rates of hydrophobic compounds weakly decrease with molecular size, it is expected that the uncertainties in the use of different models are relatively minor.[198,186,119,199] It is expected that uncertainty target for C_w would be larger than currently permitted for C_w, but other factors need to be included in uncertainty budgets including sampling uncertainty which is currently excluded. Overall, there is a need to focus on and improve each of the individual uncertainties, particularly those around the partition coefficients and sampling rate calculations completed on measured data.

While this study successfully reports data for a variety of pollutant groupings development of this area is dependent on the ongoing delivery of a number of key technical based deliverables including but not limited to;

1. Ongoing work using the co-solvent method is required in order to derive robust *Log* K_{pw} values for the compounds in question;
2. Expansion of the current suite of analytes to include all possible compounds which are legislatively required and which are applicable to PDMS;
3. New novel compounds must be included as PRCs to improve current modelling;
4. In marine applications incorporation of “salting-out” is key to reduction of UCM for PSDs;

5. Generation of clear guidance on a more “global” scale will improve overall technical performance and general comparability of generated data;
6. Further laboratory and field testing are required in order to further compare C_w values for both new and emerging analytes as well as routine compounds whereupon these can be further compared with values in other environmental compartments (*e.g.* spot samples, biota and sediment), thus supporting a continued role for PS based assessment approaches.

This applied project has demonstrated that silicone rubber PSDs have proven to be a robust monitoring tool capable of sequestering a range of contaminants and providing environmentally relevant dissolved water concentrations which can take into account seasonal changes and point source discharges. Ongoing research and development of passive sampling (and particularly in PDMS devices) will greatly support and further validate the technique for the purposes of future environmental monitoring.

7.2.2 Passive Sampling and the Legislative/Assessment Context

A great number of POPs targeted by various conventions and legislation (*e.g.* the Stockholm Convention, OSPAR and WFD) are non-polar or weakly polar, hydrophobic substances, making them ideal targets for sampling in water using PSDs.

While PSDs have been applied in a number of expansive studies (*e.g.* US Geological Survey, US Environmental Protection Agency, US National Park Service, US Fish and Wildlife Service, Virginia Department of Environmental Quality, Washington State Department of Ecology), the United Kingdom (UK Environment Agency) and the Czech Republic (Institute of Public Health) [200] in addition to having been used for trend

monitoring since 2001 at eight coastal stations in the Netherlands,[89] there is no published evidence of PSDs having already been accepted for compliance checking.

Lohmann *et al.* [147] note that legislators recognise the potentially prohibitive costs associated with incorrect management actions based on the use of potentially unrepresentative data derived from traditional sampling methods (further discussed section 2.4), thus passive sampling has a potential role in the provision of reliable and robust data that could be used in monitoring programmes on a regional and global scale.

For many POPs, regulatory limit values such as EU EQS values refer to extremely low water concentrations. Traditionally established low-volume water sampling techniques very often fail to comply with minimum performance criteria in terms of limit of quantification and measurement uncertainty, while more sensitive sampling techniques, such as high-volume sampling devices are costly and are not readily applicable for large scale monitoring programmes.

While PS is not currently recognized as being directly relevant in terms of legislative compliance it is generally recognised by the scientific community that passive sampling enables the determination of concentrations of dissolved contaminants, which is a fundamental part of an ecological risk assessment for chemical stressors. [12,201]

Levels of contaminants in Irish waters are generally low (even within more industrial areas) but some values were found to exceed the “low level BAC” as currently reported. Offshore data from the M6 platform was found to compare favourably to the low level OSPAR BAC concentrations thus indicating that this location and platform is a key ‘pristine’ site, whose data area of great value in terms of ongoing development of the

BAC process. As previously mentioned it is clear for the assessment outputs of this report that;

1. The current BAC process is very subjective to both the availability of and inclusion/exclusion of data and definition of what constitutes a "site". Guidelines on such spatial aspects would greatly focus future research programs,
2. Data are presented for a range of parameters some of which have very few examples in the literature *e.g.* PBDEs and some OCs and these data can further support BAC generation,
3. Rural or lesser impacted coastal sites are generally not readily suitable for use in the derivation of BACs, data should where possible be restricted to that obtained from (salting out corrected) offshore data,
4. The importance of M6 as a site for both the generation of an IRef and for future OSPAR BACs is clear.

As previously discussed current compliance and assessment practices are generally based on data derived from discontinuous low sampling frequency water sampling which may not provide information with required confidence and precision for compliance checking. Spot water sampling may not provide the necessary sample representativness as samples of this type give an indication of the status of the water at the moment of sampling. This is especially evident where concentrations of pollutants fluctuate on a temporal basis (*e.g.* with seasonal variation or industrial discharges). While it is clear that passive samplers such as PDMS devices may not be wholly suitable in identification of episodic pollution events (*e.g.* one off spillages etc), the technique is uniquely positioned in being able to provide time integrated data with extremely low limits of quantification for most POPs.

As research continues more reliable partition coefficient information will become available in the literature and sampling rate modelling will be further refined. Thus when combined with current knowledge in respect of analytical uncertainties, fulfilment of legally binding minimum method performance criteria and QA/QC provisions for compliance checking may be achievable using PSDs. Hence passive sampling may represent the only practicable way to monitor these substances in the water column.

7.2.3 Future Research Needs and Approaches

It is clear that there is a future role for passive samplers as both stand alone devices for the monitoring of dissolved pollutant levels for both surveillance and long term temporal monitoring of aquatic environments, the merits of such are discussed the literature and throughout this thesis. Similarly a role for passive sampling in the areas of ecotoxicological assessment and in passive dosing toxicity studies is rapidly gaining momentum.

It is well documented that PS is used to determine the chemical activity of environmental contaminants (as a function of "pollutant pressure") through measuring their freely dissolved concentrations (C_w). It has also been well reported that the C_w of hydrophobic compounds is proportional to concentrations in biota (C_{biota}) from Lohmann, [147] Smedes, [118,89] and Mayer [202], and since it is directly linked to toxicity, no normalisation for global comparability is required, and thus is a more relevant metric for environmental assessments than are "total" concentrations in water or sediments that do not relate well to toxicity (even if normalised, *e.g.* for amorphous organic carbon). The WKPSPD identified several key weaknesses of existing monitoring that can be

addressed by ongoing research efforts using PS. For biota, traditional monitoring is hampered by the diversity of organisms employed, and physiological variability in response to environmental variables; this complicates comparisons between regions, or against EAC/EQSs. Like organisms, PS devices (PSDs) accumulate contaminants over time, to similar concentrations, and with similar drivers for uptake. Both Mayer [202] and Smedes [14] have demonstrated potential mechanisms for the conversion of C_w into that determined in mussels and while differences are noted these are of the order expected from such an exercise. Further to this the ICES organized passive sampling trial (PSTS) and data from Netherlands monitoring programmes over a 10 year period both documented a clear relationship between concentrations on PCBs and PAHs in monitoring organisms and passive sampling results, [118] this concept was discussed/investigated in chapter 3. However, PS has negligible background concentrations, the derived C_w is not influenced by environmental conditions, and PS allows global comparisons. With ongoing research effort PS therefore has the potential to replace some elements of biota monitoring for hydrophobic compounds, although additional biota monitoring could still be required to assess the risks of secondary poisoning, including exposure to humans.

As detailed above the WKPSPD [197] further noted that PS of hydrophobic contaminants does not currently meet all OSPAR/EU technical requirements (*e.g.* guideline documents, assessment criteria, proficiency testing and QA/QC procedures). Ongoing research in fields such as the accurate determination of sampler-water partition coefficients are deemed crucial for a successful use of PS in monitoring programmes. It is also recommended that research continue to further enhance assessment criteria for assessment purposes, thus EAC/EQS values defined in terms of C_w would be of great value.

Following this passive dosing (PD) has been identified as an appropriate technique for generating aquatic toxicity data required for deriving EAC/EQSs expressed as C_w. Replacement of EAC/EQSs criteria in assessing hydrophobic compounds with values generated via a programme based on PS and subsequent passive dosing using (where at all possible multiple trophic level) bioassays is still in its infancy. Such data are likely to become more relevant in future years as it would then become possible to test the toxicity of suites of pollutants using relevant (multiple) assays and to then further sample the field environment and to conduct testing on the vast "cocktail" of pollutants that may be present at a particular site. Incorporation of such techniques into a wider toolkit of chemical and biological effects based assays would be informative within an integrated assessment.

There are a number of noted issues to be addressed by continued research on PD based approaches including underestimation of the effects of substances with Log Kow >5.5, since these compounds rarely attain equilibrium during the sampling stage in water. However, by including the effects of unknown (non- routinely measured) contaminants, PD approaches are still considered to be more informative than assessments based on concentrations of identified individual compounds.

WKPSPD [197] notes that passive sampling is probably better, and more practical, than biota monitoring for the purposes of both trends and compliance checking. It allows an assessment of contaminant pressure (*i.e.* chemical activity, as indicated by C_w), and does not have the many confounding factors associated with biomonitoring. However, the capability of PS to predict concentrations in prey organisms is as yet unclear. It can be expected that parallel research initiatives on PS and biomonitoring may provide

additional insights on (field based) bioaccumulation factors and contaminant transfer within the food web. Monitoring for human safety assessments (*e.g.* MSFD Descriptor 9) will continue to require the collection and analysis of biota.

Further development of each these concepts will run in parallel to ongoing development in more technical aspects of passive sampling including extension of the available partition coefficient data and future developments in the modeling of concentrations, the array of devices available for *in-situ* measurement of contaminants and in the fields of passive dosing and ecotoxicology will all become increasingly relevant in the context of wider application towards the MSFD and other ecosystem based approaches.

7.2.4 Recommendations and a Future Role for Passive Sampling

Based on the information provided throughout this study it is clear that (particularly) PDMS passive samplers are a useful technology, fit for purpose (in determining dissolved pollutant levels), straight forward and easy to use and can be deployed in the marine environment to derive dissolved water concentrations which can then subject to currently proposed conversion techniques can be used to support legislative and monitoring requirements. It is also clear that dissolved water concentrations are not currently recognised by many legislative directives opting instead for total water based assessments however given the information in current literature and within this thesis a (support) role for PS in legislative compliance monitoring is gathering pace.

PDMS in shallower coastal waters followed by SPMDs for offshore longer deployments should continue to be the passive samplers of choice for ongoing monitoring and further development of methodologies for the analysis of hydrophobic pollutants.

Internationally PDMS is rapidly becoming a favoured method for such analysis and as such is being supported by an ongoing body of validation data which is an essential component in the technique gaining acceptance as a tool for regulatory monitoring.

A role exists for SPMD devices especially where deep-sea and/or longer term deployments are envisaged. Differences in the modelling regime make this technique less favourable for “routine” 6-12 week coastal and/or freshwater deployments where PDMS is favoured.

While uptake of pollutants by PDMS is generally accepted as being broadly reflective of uptake of pollutants in biota (shellfish), continued information gathering is merited especially in investigating a role for potential relationships between passive sampling to the uptake and fate of pollutants on a wider population and ecosystem level.

Integration of PDMS sampling with biota measurements where possible should be further investigated. This may take the form of transplantation of biota (*e.g.* shellfish) to locations where PDMS are being deployed, such validation further strengthens a role for the technique. Where possible incorporation of a greater number of species (*e.g.* mussels and *nucella lapillus*) could also be co-deployed with passive samplers, with analysis of a range of “routine” pollutants in addition those exhibiting potential for monitoring (*e.g.* TBT) and monitoring of biological effects in test species (*e.g.* imposex). Such integration of passive samplers with other monitoring practices (chemical analysis and biological effects) furthers the potential role of PS in environmental/quality status monitoring.

Such integration of passive sampling into “core” monitoring regimes is recommended. As passive sampling data availability improves and the availability of partition coefficients and other supporting information is published this should lead to the development of agreed procedures for the production of appropriate assessment/reference criteria in respect of environmental protection. Only when such concrete information is available can passive sampling then be fully accepted as being of relevance in support of the goals of current legislative thresholds. On the corollary of this, once such information is available a future case can be made for legislation changes and/or parallel acceptance of passive sampling as a technique to monitor hydrophobic pollutants. Such opportunity is far less clear for polar compounds and the associated PS devices used to measure them.

On a technical level, quality assurance elements should continue to be of high priority, while laboratories analytical measurements are generally under control within defined criteria incorporating such elements into the field needs to be given equal attention. It is recommended that elements such as replicate samplers and field blanks continue to form a backbone to quality control in relation to deployments of PSDs. Further to this (and in the current absence of a proficiency scheme) it is advisable to fabricate sufficient devices to enable multiple sampling events (*e.g.* to cover a full year of sampling) so that consistency in sampler design is maintained. Following from this it is also recommended that a large scale deployment (*e.g.* >10 samplers) be completed at one test site. Upon retrieval these samplers should be frozen and then utilised on a per batch basis to further support ongoing analytical QA. Over time inter and intra batch variability statistics can then be calculated to further support validation

As recognised above the need for a development of and participation in a relevant large scale proficiency exercise for PDMS is now clear. Design of the exercise should be such that it is possible to differentiate between the influences of individual analytical methodology components (*e.g.* extraction, cleanup and analysis) in addition to the modelling methodology used.

Development of solid monitoring programme planning goals is fundamental to a measured ongoing role for passive sampling. Clear listing of the aims/goals and hypotheses in terms of how PS can be applied to support a monitoring program are vital, for example, what frequency of monitoring is required (*e.g.* placement of a buoy at a deployment site and replacement of samplers on a annual or year round to derive greater resolution). The data generated can then give an overall assessment of dissolved water concentrations present over a yearly period.

As documented throughout this thesis and further supported in the literature [147] there are some downsides (*e.g.* UCM and associated sampling rate calculations) to the use of PDMS however current evidence suggests that as research continues to further reduce uncertainty around partition coefficients and the modelling procedure that passive sampling can provide a cost effective means of delivery of low frequency sampling programs, ecotoxicologically relevant highly sensitive statistically controlled analysis in a well defined low effects matrix.

Current legislatives thresholds restrict their direct application in a legislative context, however the area is slowly gaining acceptance in the wider scientific community as being a suitable support tool in respect of legislative and monitoring requirements. This study documents the applicability of PDMS in surveillance studies and has detailed a

number of novel aspects including the application of and generation of offshore deepwater data for a variety of pollutants, the surveillance use of PDMS for the first time for the identification of (and subsequent profiling of) the combination of both PCDD/F and PCDEs in the water column this being a task which would be impracticable by conventional spot sampling techniques and thirdly the broad scale deployment of PDMS in freshwater, estuarine and coastal waters followed by assessment relative to existing criteria.

This thesis ultimately recommends pursuing the research goals detailed above and particularly in an Irish context, ongoing development of analytical methodologies to support and enable measurement of the variety of suitable compounds on legislative listings (*e.g.* PCDD/F, dicofol and heptachlor). The continued (temporal and spatial) deployment of PS devices in freshwater, estuarine and marine environments (and where feasible in offshore waters) to support assessment criteria development and ultimately the wider application of PS techniques as part of an integrated toolbox of techniques (including biological effects and chemical measurements) to further determine potential linkages between C_w and levels in other marine compartments as a means to support wider ecosystem based assessment goals is further recommended.

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Appendix A

Appendix A.1 Table 1 *Log* K_{pw} and *Log* K_{pw}^{so} values for all compounds

Appendix A.1 Table 1

Compound	Log K_{pw}	Log K_{pw}^{so}	Compound	Log K_{pw}	Log K_{pw}^{so}
Naphthalene	3.03	3.07	PCB 138	6.77	6.81
Acenaphthylene	3.26	3.30	PCB 145	6.60	6.64
Acenaphthene	3.62	3.66	PCB 149	6.60	6.64
Fluorene	3.79	3.83	PCB 153	6.72	6.76
Phenanthrene	4.11	4.15	PCB 155	6.72	6.76
Anthracene	4.21	4.25	PCB 156	6.72	6.76
Fluoranthene	4.62	4.66	PCB 180	6.99	7.03
Pyrene	4.68	4.72	PCB 170	7.10	7.14
Chrysene	5.25	5.29	PCB 194	7.43	7.47
Benzo(a)anthracene	5.32	5.36	PCB 204	7.75	7.79
Benzo(b)fluoranthene	5.74	5.78	PCB 209	7.81	7.85
Benzo(k)fluoranthene	5.74	5.78	PCB	4.6	4.64
Benzo(a)pyrene	5.69	5.73	HCB	5.04	5.08
Indeno(1,2,3-cd)pyrene	6.06	6.10	a-HCH	3.28	3.32
Dibenzo(a,h)anthracene	6.24	6.28	b-HCH	3.29	3.33
Benzo(g,h,i)perylene	6.02	6.06	g-HCH	3.34	3.38
Naphthalene $_{-d8}$	3.02	3.06	d-HCH	2.81	2.85
Acenaphthene $_{-d8}$	3.57	3.61	HCBD	4.91	4.95
Phenanthrene $_{-d10}$	4.06	4.10	Chlorofenvinphos-cis	4.59	4.63
Chrysene $_{-d12}$	5.2	5.24	-trans	4.86	4.90
Perylene $_{-d12}$	5.49	5.53	a-Endosulfan	4.85	4.89
Acenaphtylene$_{-d8}$	3.21	3.25	op-DDE	6.16	6.20
Anthracene$_{-d10}$	4.16	4.20	pp-DDE	6.26	6.30
Pyrene $_{-d12}$	4.63	4.67	op-DDD	5.52	5.56
Benzo(a)anthracene$_{-d12}$	5.27	5.31	pp-DDD	5.41	5.45
Benzo(a)pyrene $_{-d12}$	5.64	5.68	op-DDT	6.27	6.31
			pp-DDT	6.14	6.18
PCB 4	4.36	4.40	Dieldrin	5.26	5.30
PCB 18	5.23	5.27	cis-chlordane	5.24	5.28
PCB 28	5.53	5.57	transchlordane	5.24	5.28
PCB 31	5.53	5.57			
PCB 44	5.82	5.86	BDE 28	5.74	5.78
PCB 52	5.80	5.84	BDE 47	6.2	6.24
PCB 55	5.98	6.02	BDE 99	6.64	6.68
PCB 78	6.08	6.12	BDE 100	7.13	7.17
PCB 101	6.28	6.32	BDE 153	7.84	7.88
PCB 105	6.42	6.46	BDE 154	7.75	7.79
PCB 118	6.42	6.46	BDE 183	8.23	8.27

Appendix A.2 Additional Literature Review Passive sampler information

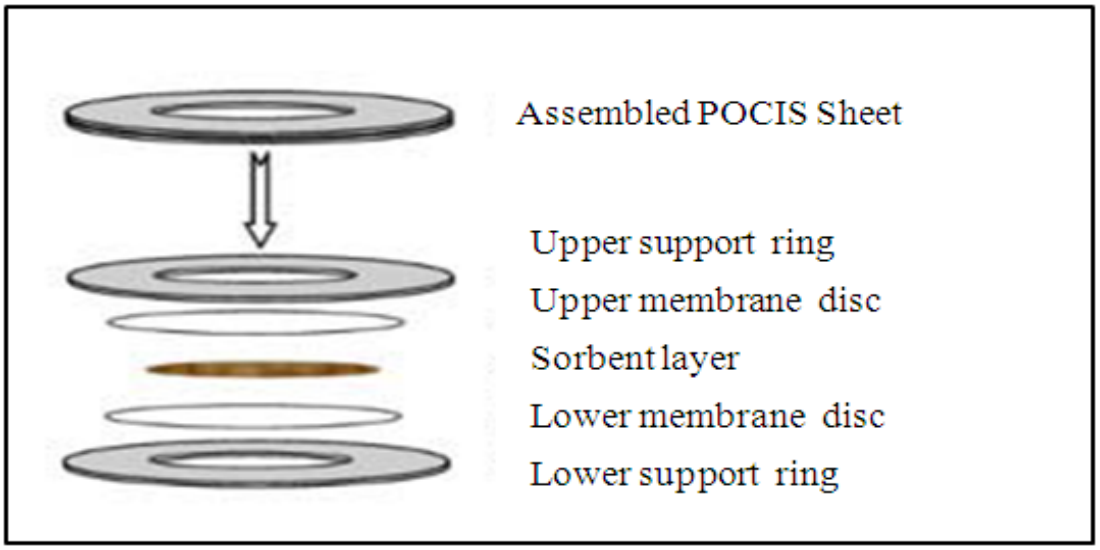
A.2.1 Polar Organic Chemical Integrative Sampler (POCIS)

As well as work on the hydrophobic compounds, already discussed in this study, work has also been undertaken to passively sample hydrophilic compounds (HpOCs) in the marine environment. The POCIS has been used to sample for a wide range of compounds including some pesticides, prescription and non-prescription drugs, personal care and consumer products, industrial and domestic use chemicals and their degradation products.[203,204,205] Evidence is growing that large scale fluxes of these more environmentally friendly compounds are responsible for incidences of acute toxicity and sub-lethal chronic abnormalities including neurotoxicity and severely impaired reproduction.[206,205] Of the compounds mentioned above, pharmaceutical compounds which can enter the environment can be of particular concern due to their diverse pharmacological responses. These HpOCs can enter the environment mainly through treated effluents from wastewater treatment plants and direct disposal of unused drugs.[203]

Traditional sampling methods have been upgraded with the use of SPE (solid phase extraction) cartridges however the drawbacks of traditional sampling still remain in that large volumes of water are sometimes need and sensitivity is an issue. Passive samplers can offer an attractive alternative to the traditional methods of water collection and analysis. The POCIS has been envisioned to offer the possibility of detection of HpOCs at low levels in the environment.[203]

A.2.1.1 POCIS Description and Rationale

The POCIS passive sampler has been shown to accumulate compounds with a Log K_{ow} value of < 3.5 which are not accumulated to any degree in the other types of passive sampler mentioned in this study.[203,207] The POCIS consists of a two polyethersulphone (PES) membranes, between which is 'sand wiched' a sheet of solid-phase sorbent or mixture of sorbents. Because the PES membranes are not amenable to annealing the structure is compressed around a frame which comprises a series of rings which, when a compression seal is formed, prevents the loss of the sorbent. This 'membrane-sorbent-membrane sand wich' is the functional aspect of the device and the cage is used primarily as a means of orientation and support of the sampler. *Figure A1* below shows the view of the membrane sand wich of one POCIS sheet.



Appendix A.2 Figure 1 view of a single POCIS 'sand wich' many of which are attached to the sampler cage, reproduced from Alvarez *et al.* [207]

The PES membrane is porous and acts as a semipermeable barrier through which the dissolved HpOCs present in the environment pass to interact with the sorbent layer. Once deployed and immersed the water permeates the pore structure of the PES membrane allowing direct interaction of any contaminants present with the sorbent

where they can be accumulated. The PES membrane does not allow interaction of particulate matter, microorganisms or macromolecules with the sorbent phase and has been found to be more resistant to bio-fouling than other polymeric compounds used as barriers in passive sampling devices.[203] The POCIS design is versatile in that the sorbents used in different layers in the overall device can be changed to target specific classes of compound.[207,208] Once a compound can interact with the sorbent it is sequestered as the sorbent acts as an infinite sink allowing the accumulation of contaminants for approximately 30 days.[208]

A.2.1.2 POCIS Theory

The accumulation of contaminants by the POCIS passive sampler generally follows first order kinetics which is characterised by a linear uptake phase followed by a gradual change as the sampler comes into the equilibrium phase with the surrounding environment.[203] Generally to derive dissolved water concentrations of passive samplers the use of PRCs is required to estimate site specific sampling rates for the compounds present. In the case of POCIS the nature of the sorbent *i.e*. an infinite sink, means that any PRC compound spiked into the sampler before deployment is unlikely to dissipate meaning that the sampling rate cannot at present be calculated. This is one of the major drawbacks of the POCIS design however it is reported as an excellent screen for the compounds of interest.[132, 209, 210] Huckins *et al.* [211] formulated the following equations for the linear uptake phase of the POCIS (*Eqn.A1*):

$$C_w = \frac{C_s M_s}{R_s t} \qquad \text{Eqn.A1}$$

Where C_w and C_s are the analyte concentration in the water and in the sampler respectively and m_s is the mass of the sorbent with t being the time in days. The sampling rate formulation changes slightly depending whether the uptake is controlled by the membrane, or the water boundary layer. The flowing two equations describe how the R_s is calculated when the uptake is water boundary layer controlled (*Eqn.A2*) and membrane controlled (*Eqn.A3*):

$$R_s = \left(\frac{D_w}{\delta_w}\right)A \qquad \text{Eqn.A2}$$

$$R_s = \left(\frac{D_m}{\delta_m}\right)K_{mw}A \qquad \text{Eqn.A3}$$

Where D w and D_m describe the diffusion coefficient in water (w) and in the membrane (m), δ_w and δ_m is the effective thickness of the WBL and the hydrated membrane, A is the surface area of the sampling device with K_{mw} describing the equilibrium membrane-water partition coefficient. Sampling rates for selected chemicals have been determined using the static renewal design the details of which are described by Alvarez *et al.* [212]

A.2.1.3 POCIS Use

POCIS samplers once prepared are transported to the site in a solvent rinsed air tight container such as a paint can. It can then be deployed and upon retrieval the POCIS membrane is washed gently with a soft brush and running water to ensure no perforation of the disc and contamination of the sorbent. The cage is disassembled and the sheets separated with the sorbent being transferred to a suitable organic solvent *e.g.* methanol. The eluant is then cleaned up using column chromatography and dried down

until it is in a suitable volume for instrumental analysis. POCIS extracts have been fractionated for analysis of different components and the extracts have also been subjected to various bioassay techniques such as the yeast estrogen screen (YES) and yeast androgen screen (YAS).[203] POCIS has been used as a screen for pharmaceuticals including Acetaminophen and Carbamazepine, for illicit drugs including methamphetamine and MDMA, and synthetic hormones such as 17β-Estradiol and 17ά-Ethynylestradiol. It has also been used to screen for some polar pesticides such as Chlorpyrifos and Diuron.

A.2.2 Diffusive Gradients in Thin Films (DGT)

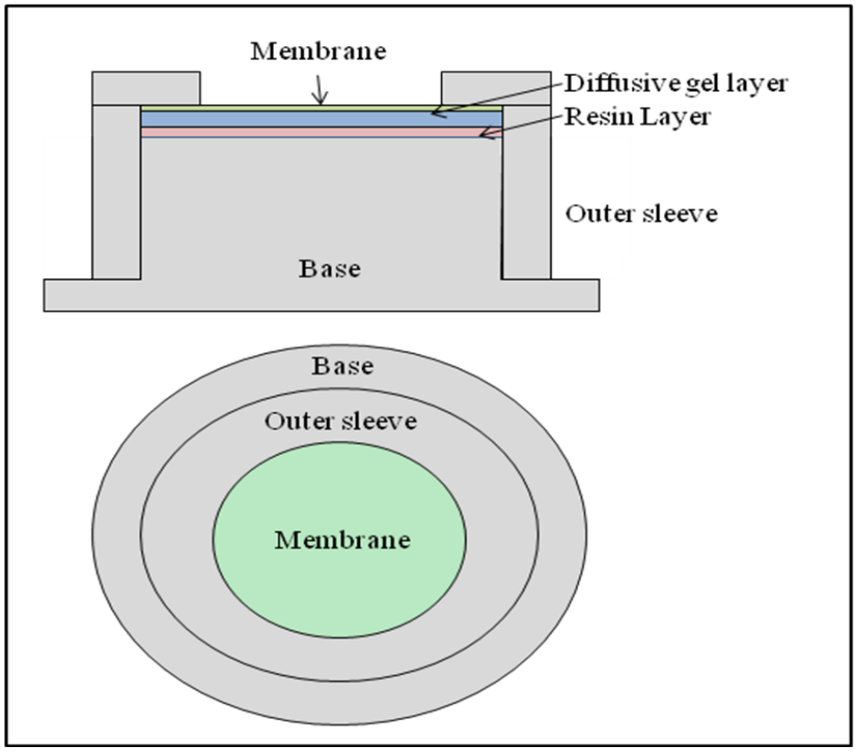
In conjunction with the development of PSDs for the accumulation and analysis of organic contaminants in the marine environment, various devices have been developed for the analysis of trace metal species in water. One of these samplers has been the DGT which was first used in the mid – 1990s as an *in-situ* technique for detection of trace metal species.[213, 214] Since then it has been developed as a general tool for monitoring a wide range analytes including transition and heavy metals.[215] DGT relies on the diffusion of solutes across a well defined gradient typically established within a layer of hydrogel and an outer filter membrane. The filter membrane is directly exposed to the sampled media allowing analytes of interest to cross into the sampler excluding particulate matter. Once a solute has diffused through the filter membrane it is irreversibly sequestered or chelated by a binding agent, typically ‘Chelex 100’ which is immobilised in a second layer of hydrogel.

DGT has been used to sample for a wide range of analytes including Al, Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn, Ca and Mg. To measure mercury it was found that a change in

composition of the hydrogel allowed Hg to be accumulated.[216] It has also been shown that the typical DGT sampler set up could be used to measure Cr(III) but not Cr(VI) and also Cs and Sr along with many other heavy and transition metals.

A.2.2.1 DGT Description and Rationale

The DGT system consists of a base and a cap which contains the filter membrane, diffusive gel layer and the resin. *Figure A2* below shows the basic structure of the DGT.



Appendix A.2 Figure 3 Schematic drawing of the DGT passive sampler. Reproduced from Zhang *et al.* [214]

Once immersed in the sampled medium the membrane is exposed allowing diffusion of chemically labile metal species across the membrane where they are accumulated by a selective binding agent. Generally the binding agent used is 'chelex 100' which is immobilised in a polyacrylamide hydrgel, however varying the binding agent and hydrogel can allow a variety of metal species to be accumulated. DGT are characterized

by rapid accumulation of metal species. They can be left *in-situ* for short periods (1 day) or for up to 3 months until the receiving phase becomes saturated.

A.2.2.2 DGT Theory

After deployment of the DGT sampler the diffusive flux (F) of an ion is given by Fricks first law of diffusion[215] where dC/Dx is the change in concentration (g cm^{-3}) that occurs over a distance x (cm) which is given by the following equation (*Eqn A4*):

$$F = D_0 \frac{dC}{dx} \qquad \text{Eqn.A4}$$

D_0 is the diffusion coefficient which is measured at infinite dilution and at a reference temperature of 25^{o}C but can be corrected to any temperature by applying the Stokes-Einstein equation where T_0 and T_t are measure in Kelvin (*Eqn.A5*):

$$\frac{D_0 \eta_0}{T_0} = \frac{D_t \eta_t}{T_t} \qquad \text{Eqn.A5}$$

Where η_0 is the viscosity of water which can by expressed using the following equation (*Eqn.A6*) at a reference temperature of 25^{o}C and η_t is the *in-situ* temperature of the water:

$$\log \frac{\eta_0}{\eta_t} = \frac{1.37023(t-25) + 8.36e^{-04}(t-25)^2}{109 + t} \qquad \text{Eqn.A6}$$

In DGT the diffusion of metal ions in the diffusive layer gel (D_{Gel}) can be approximated by 0.85 x D. At steady state the concentration gradient (dC/dx) is the difference between

the bulk solution concentration and the concentration at the interface between the diffusive and resin layer, C', which is zero depending on the ability of the resin layer to act as an infinite sink. The distance x is the diffusional path length through all DGT layers and the diffusive boundary layer (DBL). Assuming the DBL is minimal and that the diffusive coefficient for the other layers with a combined thickness (Δg) is the same a simplified explanation of the relationship is shown in *Eqn.A7*

$$F = \frac{D_{Gel}(C - C')}{\Delta g} \qquad \text{Eqn.A7}$$

The mass of the metal accumulated by the resin gel, M is then calculated by placing the gel into a known volume of elution acid (V_e). The volume of the gel layer, V_{Gel} is taken as 0.16 mL for a common DGT sampler which is 8 mm thick and f_e is elution efficiency:

$$M = \frac{C_e(V_{Gel} + V_e)}{f_e} \qquad \text{Eqn.A8}$$

Substitution of f in the equation above (*Eqn.A.8*) means the bulk concentration measured by DGT (C_{DGT}) can be calculated by the following equation (*Eqn.A9*):

$$C_{DGT} = \frac{M\Delta g}{D_{Gel} t\Delta} \qquad \text{Eqn.A9}$$

A.2.2.3 DGT Use

As an alternative to logistically and analytically demanding spot sampling techniques DGT can be used to carry out routine monitoring for metals in the marine environment. Successful deployment in the marine environment depends on the absence of possible metal contamination sources like chains etc. Polypropylene ropes and buoys have been used for many deployments of DGT in the environment.[18] The diffusive gel most commonly used in the preparation of DGT is a polyacrylamide gel cross-linked with and agarose derivative referred to APA2. The procedures used in the preparation of APA2 have been discussed in many publications [217, 214, 213] and so will not be discussed in detail here. Once the gel has been prepared it is then cast between two acid washed plates and placed in an oven at 45^{o}C for 1 hour before being deionised and placed in the DGT apparatus for deployment.[215]

A.2.3 Chemcatcher

Chemcatcher is an integrative passive sampler consisting of a C_{18} Empore® disk receiving phase saturated with *n*-octanol and fitted with low-density polyethylene diffusion membrane which is housed in a reusable PTFE shell which can be calibrated for the measurement of time-weighted average concentrations of hydrophobic micropollutants, including PAHs, PCBs and OCs, in the marine environment.[30] The original design of the chemcatcher was envisioned to provide a low cost sampling body which could house a range of different sampling configurations depending on the analytes to be sampled. A wide range of receiving phases and diffusion films have been used including those which allow the chemcatcher to sample metallic and organometallic species in the marine environment.[218,219] As with all PSDs the accumulation of contaminants from the surrounding environments into the sampling

device occurs as a result of the chemically favourable adsorbent receiving phase. Selected analytes permeate through the diffusion membrane phase before being adsorbed or absorbed onto the receiving phase. [218]

A.2.3.1 Chemcatcher Description and Rationale

The chemcatchers versatility as a PSD is due to nature and realisation of its design. The body of the chemcatcher is manufactured from PTFE which is dense in comparison to water allowing the sampler be deployed easily. [218] PFTE has a low sorption capacity for most environmental pollutants allowing it to be used to sample a wide variety of contaminants.[105] Finally PTFE is a robust material for use in the marine environment meaning it can be reused a number of time which keeps the cost of the system to a minimum. The rate of diffusion of analytes from the bulk water to the receiving phase is proportional to the surface area over which diffusion takes place and inversely proportional to the diffusion path length, therefore the physical dimensions of the sampler body will significantly affect the sampling rate for different analytes. [220] The body of the Chemcatcher was optimised in terms of both materials of construction and geometry with the PTFE body constructed to fit a 47 mm Empore disk receiving phase, having an active sampling area of 17.5 cm^2. [100] The diffusion membrane used for the chemcatcher again depends on the nature of the analyte to be sampled with LDPE being used in many cases to sample for hydrophobic contaminants while a CA (cellulose acetate) membrane can be used for inorganic species. [221]

In calibration experiments the effect of physicochemical properties *e.g.* compound hydrophobicity, hydrodynamics and water temperature on kinetic and thermodynamic parameters which characterise the diffusion of analytes between the sampler and the surrounding medium were investigated and it has been found that the rate of uptake of

test analytes from water to the sampler receiving phase is related to the rate at which they offload to the water.[105, 220] This enables the use of off-loading rates of performance reference compounds (PRCs) preloaded on to the receiving phase to be used to adjust uptake rates for the effects of temperature and hydrodynamic conditions in the field. [218]

A.2.3.2 Chemcatcher Theory

The theory of chemcatcher operation in the marine environment follows the general passive sampler laws as explained in section 2.2. In summary, mass transfer of an analyte from the surrounding medium to the receiving phase in the sampler involves interaction of the analyte with several diffusion and interfacial barriers. [218] In the initial exposure stage analyte uptake is expected to be linear or time-intergrative after steady state flux of chemicals has been achieved.[222, 223] Uptake of contaminants in the liner phase can be described by the following formula:

$$m_D(t) = m_0 + C_W R_s t \qquad \text{Eqn.A10}$$

Where m_D is the amount of the analyte accumulated in the receiving phase, m_0 is the initial amount of analyte in the receiving phase and R_s is the sampling rate. [218] R_s can be described using the following formula:

$$R_s = k_{ov} A \qquad \text{Eqn.A11}$$

Where k_{ov} (m s^{-1}) is the overall mass transfer coefficient and A is the surface area of the sampler membrane. Uptake of contaminants from the surrounding medium to the receiving phase can be considered linear in nature until the concentration factor of the

sampler reaches half saturation ($m_D(t)/C_W$) after which a curve-linear or equilibrium. The chemcatcher has been shown to be a usefull PSD in the analysis of both dissolved metals and a variety of pesticides and other organic contaminants found in the marine environment primarily due to the interchangeable nature of its membrane and receiving phase which makes the chemcatcher a versatile sample and of importance in a 'toolbox' of samplers for the marine environment.

Appendix A.3 GC-ECD and GC-MS Instrumentation Parameters

The Instrumental parameters used to analyse POPs using the GC-MS are described in the following tables (Appendix A.3 *Table 1* and *Table 2*) with the GC-ECD instrumental set up discussed in section 3.2.2.

Appendix A.3 Table 1 Instrumental parameters used to analyse PCB and PAH compounds using the Agilent 6890 gas chromatogram coupled to a 5973N mass spectrum GC-MS

				SIM Segment				
Compound	**Ion**	**Rt**	**ISTD**	**Segment**	**Start time (Min)**			
PAHs								
Naphthalene	128	8.81	naphthalene d_8	1	8.00		Type	Splitless
Acenaphthylene	152	12.38	acenaphthene d_{10}	2	11.00	**Injector**	Temp (°C)	250
Acenaphthene	153	12.82	acenaphthene d_{10}	3	12.60		volume(µL)	5
Fluorene	166	14.09	acenaphthene d_{10}	4	13.50	**Carrier**	gas	helium
Phenanthrene	178	16.96	phenenthrene d_{10}	5	15.00	**Gas**	Flow (ml/min)	1
Anthracene	178	17.22	phenenthrene d_{10}				Method	EI
Fluoranthene	202	22.14	phenenthrene d_{10}	6	22.00	**Detector**	Ion source temp (°C)	230
Pyrene	202	23.36	phenenthrene d_{10}				Auxillary temp(°C)	300
Chrysene	228	31.87	chrysene d_{12}	7	28.00	**Column**	Agilent DB5-60 m x	
Benzo(a)anthracene	228	32.20	chrysene d_{12}				0.25 mm x 0.25µm	
Benzo(b)fluoranthene	252	41.18	chrysene d_{12}	8	37.00			
Benzo(k)fluoranthene	252	41.42	chrysene d_{12}					
Benzo(a)pyrene	252	43.90	chrysene d_{12}					
Indeno(1,2,3-cd)pyrene	276	55.29	perylene d_{12}	9	47.00			
Dibenzo(a,h)anthracene	278	55.75	perylene d_{12}					
Benzo(g,h,i)perylene	276	58.09	perylene d_{12}					
PCBs								
PCB 18	256	11.39	PCB 112	1	11.00		Type	Splitless
PCB 28	256	12.20	PCB 112	2	12.00	**Injector**	Temp (°C)	280
PCB 31	256	12.25	PCB 112				volume(µL)	3
PCB 52	292	12.86	PCB 112	3	12.70	**Carrier**	gas	helium
PCB 44	292	13.67	PCB 112			**Gas**	Flow (ml/min)	1.4
PCB 101	326	15.11	PCB 112				Method	EI
PCB 149	360	17.17	PCB 112	4	16.50	**Detector**	Ion source temp (°C)	230
PCB 118	326	17.18	PCB 112				Auxillary temp(°C)	300
PCB 153	360	18.28	PCB 112			**Column**	SGE-HT8 50 m x 0.25mm	
PCB 105	360	19.84	PCB 112				x 0.22µm	
PCB 138	360	20.50	PCB 112					
PCB 156	360	23.76	PCB 112	5	23.00			
PCB 180	394	23.99	PCB 112					
PCB 170	393	27.38	PCB 112					
PCB 194	430	31.85	PCB 112	6	30.00			
PCB 209	498	37.96	PCB 112					

ISTD – Internal standard.

Appendix A.3 Table 2 Instrumental parameters used to analyse OC and PBDE compounds using the Agilent 6890 gas chromatogram coupled to a 5973N mass spectrum GC-MS

				SIM Segment				
Compound	**Ion**	**Rt**	**ISTD**	**Segment**	**Start time (Min)**			
OCs								
HCBD	225	10.46	PCB 112	1	10.00		Type	Splitless
HCB	284	18.45	PCB 112	2	16.00	**Injector**	Temp (^{o}C)	280
a-HCH	181	18.74	PCB 112				volume(µL)	3
g-HCH	181	19.75	PCB 112			**Carrier**	gas	helium
b-HCH	181	20.22	PCB 112			**Gas**	Flow (ml/min)	1.4
Heptachlor	272	20.62	PCB 112	3	20.20		Method	EI
d-HCH	219	21.22	PCB 112			**Detector**	Ion source temp (^{o}C)	230
aldrin	263	21.68	PCB 112	4	21.50		Auxillary temp(^{o}C)	300
Oxychlordane	387	23.15	PCB 112			**Column**	SGE HT-8 50 m x 0.22mm	
Heptachlor epoxide	353	23.77	PCB 112	5	23.50		x 0.25µm	
Transnonachlor	409	24.66	PCB 112	6	24.00			
Transchlordane	373	24.61	PCB 112					
op-DDE	246	24.92	PCB 112	7	24.85			
Cischlordane	373	25.19	PCB 112					
pp-DDE	246	26.23	PCB 112	8	25.40			
Dieldrin	263	27.14	PCB 112	9	27.00			
op-DDD	235	27.65	PCB 112	10	29.00			
op-DDT	235	29.48	PCB 112					
pp-DDD	235	29.89	PCB 112					
pp-DDT	235	31.93	PCB 112			**Column**	SGE HT-8 50 m x 0.22mm	
							x 0.25µm	
PBDE							Type	Splitless
BDE28	406	12.56	PCB 112	1	11.00	**Injector**	Temp (^{o}C)	300
BDE47	486	14.15	PCB 112	2	13.00		volume(µL)	5
BDE100	404	17.12	PCB 112	3	16.00	**Carrier**	gas	helium
BDE99	404	18.2	PCB 112			**Gas**	Flow (ml/min)	2
BDE154	484	22.5	PCB 112	4	20.00		Method	EI
BDE153	484	23.65	PCB 112			**Detector**	Ion source temp (^{o}C)	230
BDE183	721	36.66	PCB 112	5	30.00		Auxillary temp(^{o}C)	300

ISTD – Internal Standard

Appendix A.4 GC-ECD and GC-MS Instrumental Validation Data.

Appendix A.4 Table 1. Method validation results relating to GC-MS PAH and GC-ECD OC/PCB method validation including specificity, accuracy, precision, linearity and limit of detection/quantification as well as UCM % based on replicate measurements of QOR099BT (n=17).

	Specificity (min)			Accuracy (ng/g)			Precision				Linearity	LOD/LOQ (ng/g)		
Compound	1	2	3				Average Recovery (ng/g)	Standard Deviation	% RSD	Range	(<0.995)	LOD	LOQ	UCM %
				STD 2	STD 5	STD 9								
Naphthalene	8.80 (0.002)	8.81 (0.002)	8.81 (0.002)	499.13 (1.73)	60.62 (0.59)	3.95 (0.22)	500.48	3.22	0.64	496.24 - 507.41	0.999	0.280	0.653	
Acenaphthylene	12.38 (0.003)	12.38 (0.004)	12.38 (0.002)	499.87 (1.73)	62.16 (0.58)	4.45 (0.13)	501.84	2.38	0.47	498.60 - 505.95	0.999	0.004	0.010	
Acenphthene	12.82 (0.003)	12.82 (0.003)	12.82 (0.002)	501.26 (0.23)	62.72 (1.50)	4.12 (0.20)	501.76	3.06	0.61	495.86 - 506.82	1.000	0.018	0.041	23.6
Fluorene	14.08 (0.002)	14.09 (0.003)	14.09 (0.002)	499.97 (1.58)	60.36 (0.81)	4.42 (0.18)	502.18	1.9	0.38	499.30 - 505.37	0.999	0.013	0.029	27.8
Phenanthrene	16.94 (0.004)	16.94 (0.003)	16.94 (0.001)	501.25 (1.07)	64.85 (0.23)	3.93 (0.06)	499.6	2.96	0.59	495.01 - 504.55	1.000	0.005	0.012	23.6
Anthracene	17.10 (0.003)	17.10 (0.004)	17.10 (0.002)	500.77 (1.76)	59.87 (1.14)	4.23 (0.08)	504.32	2.04	0.41	500.55 - 506.59	0.999	0.005	0.011	17.5
Fluoranthene	22.11 (0.004)	22.11 (0.006)	22.11 (0.003)	500.81 (1.43)	59.81 (1.24)	4.32 (0.08)	501.04	3.27	0.65	495.22 - 505.94	0.999	0.003	0.006	19.5
Pyrene	23.34 (0.004)	23.34 (0.005)	23.33 (0.003)	500.28 (3.95)	59.62 (0.54)	4.45 (0.03)	500.92	2.98	0.59	497.20 - 506.41	0.999	0.003	0.007	14.8
Chrysene	31.85 (0.010)	31.85 (0.008)	31.84 (0.006)	501.33 (2.75)	62.07 (2.17)	4.05 (0.09)	502.61	4.27	0.85	497.20 - 506.41	0.998	0.004	0.010	40.8
Benzo(a)anthracene	32.17 (0.006)	32.17 (0.008)	32.17 (0.006)	503.09 (0.29)	64.54 (0.84)	4.15 (0.01)	502.62	2.44	0.48	499.67 - 507.27	0.998	0.007	0.016	21.4
Benzo(b)fluoranthene	41.18 (0.010)	41.18 (0.007)	41.17 (0.005)	498.53 (2.09)	59.28 (0.73)	4.00 (0.03)	501.07	3.24	0.65	496.82 - 505.71	0.998	0.004	0.009	30.6
Benzo(k)fluoranthene	41.39 (0.011)	41.38 (0.009)	41.38 (0.008)	499.43 (0.75)	58.34 (0.52)	4.16 (0.06)	501.33	3.43	0.68	496.60 - 506.45	0.998	0.003	0.008	12.7
Benzo(a)pyrene	43.90 (0.015)	43.89 (0.009)	43.89 (0.007)	498.36 (4.27)	59.97 (1.51)	4.32 (0.12)	502.03	2.49	0.5	498.72 - 506.23	0.998	0.003	0.008	18.8
Indeno(1,2,3-c,d)pyrene	55.26 (0.027)	55.25 (0.014)	55.24 (0.011)	498.27 (1.30)	62.53 (1.92)	4.02 (0.03)	502.31	2.65	0.53	496.14 - 505.20	0.999	0.003	0.007	40.4
Benzo(g,h,i)perylene	55.75 (0.030)	55.73 (0.013)	55.73 (0.013)	501.23 (2.99)	60.50 (1.98)	3.50 (0.16)	502.16	2.28	0.45	499.35 - 505.67	0.999	0.002	0.005	26.8
Dibenzo(a,h)anthracene	58.08 (0.025)	58.06 (0.018)	58.06 (0.017)	500.97 (2.15)	59.22 (0.29)	3.63 (0.14)	498.15	3.29	0.48	495.95 - 503.37	0.999	0.003	0.007	41.4
				STD 2	STD 4	STD 7								
HCB	10.66 (0.003)	10.64 (0.011)	10.64 (0.002)	20.74 (0.17)	5.69 (0.14)	0.035 (0.004)	2.08	0.03	1.5	2.03 - 2.12	0.996	0.005	0.011	37.9
PCB 18	12.66 (0.015)	12.62 (0.024)	12.62 (0.007)	20.66 (0.28)	5.28 (0.05)	0.036 (0.000)	1.90	0.03	1.8	1.85 - 1.97	0.996	0.006	0.013	
PCB 31	14.86 (0.006)	14.81 (0.014)	14.83 (0.003)	20.89 (0.10)	5.34 (0.04)	0.035 (0.003)	1.89	0.03	1.7	1.85 - 1.94	0.998	0.005	0.011	12.2
PCB 28	14.91 (0.026)	14.91 (0.010)	14.91 (0.010)	21.09 (0.11)	5.46 (0.05)	0.037 (0.001)	1.93	0.04	2.1	1.90 - 2.03	0.998	0.007	0.015	17.0
PCB 52	16.84 (0.011)	16.81 (0.025)	16.80 (0.005)	20.40 (0.03)	5.25 (0.07)	0.036 (0.001)	1.89	0.04	2.1	1.83 - 1.97	0.998	0.005	0.011	12.8
PCB 44	18.37 (0.022)	18.36 (0.021)	18.35 (0.005)	20.67 (0.10)	5.36 (0.08)	0.034 (0.004)	1.90	0.03	1.6	1.85 - 1.94	0.998	0.004	0.010	
PCB 101	22.24 (0.007)	22.20 (0.041)	22.20 (0.004)	20.97 (0.19)	5.44 (0.05)	0.033 (0.004)	1.94	0.03	1.3	1.89 - 1.98	0.999	0.005	0.011	6.5
PPDDE	24.76 (0.005)	24.73 (0.028)	24.71 (0.008)	20.65 (0.13)	5.44 (0.02)	0.036 (0.005)	1.95	0.02	1.0	1.92 - 1.99	0.998	0.001	0.003	31.0
PCB 149	26.69 (0.033)	26.65 (0.034)	26.63 (0.005)	20.85 (0.07)	5.45 (0.08)	0.038 (0.002)	1.98	0.02	1.2	1.95 - 2.02	0.999	0.005	0.012	
PCB 118	27.19 (0.010)	27.16 (0.029)	27.15 (0.002)	21.14 (0.18)	5.58 (0.04)	0.038 (0.003)	2.00	0.02	1.2	1.97 - 2.03	0.999	0.005	0.011	12.1
PCB 153	28.34 (0.018)	28.29 (0.041)	28.28 (0.004)	21.16 (0.22)	5.62 (0.05)	0.039 (0.003)	2.03	0.02	0.9	2.00 - 2.06	0.999	0.004	0.010	5.8
PCB 105	29.75 (0.026)	29.69 (0.035)	29.69 (0.013)	20.60 (0.09)	5.50 (0.04)	0.041 (0.002)	1.96	0.02	1.1	1.94 - 1.99	0.999	0.005	0.011	15.2
PCB 138	30.94 (0.009)	30.90 (0.032)	30.90 (0.008)	21.07 (0.27)	5.63 (0.04)	0.036 (0.001)	2.01	0.02	0.8	1.99 - 2.04	0.998	0.005	0.012	20.6
PCB 156	34.62 (0.011)	34.60 (0.026)	34.58 (0.006)	20.63 (0.24)	5.63 (0.05)	0.038 (0.001)	2.06	0.02	1.1	2.02 - 2.09	0.998	0.004	0.010	19.1
PCB 180	35.16 (0.012)	35.14 (0.029)	35.12 (0.004)	20.48 (0.36)	5.66 (0.05)	0.040 (0.004)	2.10	0.02	1.0	2.06 - 2.13	0.998	0.005	0.012	14.0
PCB 170	37.03 (0.009)	37.02 (0.009)	37.00 (0.013)	20.67 (0.24)	5.64 (0.06)	0.037 (0.003)	2.04	0.02	1.0	1.99 - 2.07	0.998	0.004	0.009	
PCB 194	40.07 (0.008)	40.05 (0.018)	40.05 (0.004)	20.79 (0.13)	5.54 (0.07)	0.035 (0.002)	2.00	0.02	1.0	1.96 - 2.03	0.997	0.010	0.019	
PCB 209	42.53 (0.008)	42.52 (0.023)	42.50 (0.004)	20.91 (0.20)	5.59 (0.08)	0.038 (0.002)	2.00	0.02	0.9	1.97 - 2.02	0.998	0.010	0.019	

Appendix A.4. Table 2 Example, using PCB data generated from the GC-MS of how instrumental LOD/LOQ values are calculated using repeated analysis of procedural blanks.

													Instrumental	
Compound ng/g	1	2	3	4	5	6	7	8	9	10	11	Average	STDEV	LOD	LOQ
PCB 18	0.001	0.002	0.004	0.001	0.001	0.000	0.000	0.004	0.005	0.000	0.000	0.002	0.002	0.006	0.013
PCB 31	0.002	0.002	0.004	0.001	0.001	0.004	0.004	0.005	0.004	0.003	0.000	0.003	0.002	0.005	0.011
PCB 28	0.000	0.000	0.002	0.007	0.002	0.003	0.003	0.005	0.001	0.002	0.000	0.002	0.002	0.007	0.015
PCB 52	0.000	0.004	0.003	0.001	0.002	0.003	0.002	0.005	0.001	0.001	0.000	0.002	0.002	0.005	0.011
PCB 44	0.000	0.000	0.001	0.000	0.005	0.001	0.000	0.001	0.000	0.000	0.000	0.001	0.001	0.004	0.010
PCB 101	0.001	0.002	0.001	0.006	0.001	0.002	0.002	0.002	0.000	0.002	0.003	0.002	0.002	0.005	0.011
PCB 149	0.002	0.004	0.008	0.003	0.003	0.002	0.005	0.005	0.003	0.003	0.004	0.004	0.002	0.005	0.012
PCB 118	0.005	0.003	0.000	0.002	0.001	0.004	0.001	0.003	0.003	0.003	0.001	0.002	0.002	0.005	0.011
PCB 153	0.003	0.003	0.000	0.004	0.003	0.005	0.004	0.003	0.002	0.004	0.001	0.003	0.001	0.004	0.010
PCB 105	0.003	0.004	0.005	0.003	0.004	0.007	0.002	0.001	0.004	0.004	0.003	0.004	0.002	0.005	0.011
PCB 138	0.003	0.004	0.000	0.004	0.002	0.004	0.001	0.004	0.000	0.001	0.001	0.002	0.002	0.005	0.012
PCB 156	0.003	0.003	0.003	0.005	0.003	0.002	0.002	0.000	0.002	0.000	0.002	0.002	0.001	0.004	0.010
PCB 180	0.004	0.003	0.000	0.003	0.005	0.000	0.003	0.004	0.001	0.002	0.004	0.003	0.002	0.005	0.012
PCB 170	0.000	0.002	0.000	0.000	0.004	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.001	0.004	0.009

STDEV – Standard deviation.

Appendix A.4 Table 3 Example of UCM calculation, using the Nordtest method and QUASIMEME material QOR099BT (n=17) for PCBs

Compound ng/g	Average value	Assigned	STDEV	% RSD	Total error%	Error	Bias %	U(Cref)	Relative U(Cref)	U bias	U_C	UCM
PCB 31	0.187	0.19	0.011	5.83	19	0.04	1.3	0.02	9.7	1.74	6.09	12.2
PCB 28	0.223	0.23	0.018	7.89	18	0.04	3.0	0.02	9.2	3.17	8.50	17.0
PCB 52	0.586	0.6	0.035	5.91	14.6	0.09	2.3	0.04	7.4	2.48	6.41	12.8
PCB 101	2.576	2.57	0.081	3.16	13	0.33	0.2	0.17	6.6	0.82	3.26	6.5
PCB 118	1.998	1.98	0.119	5.93	13.1	0.26	0.9	0.13	6.7	1.21	6.06	12.1
PCB 153	7.503	7.56	0.198	2.65	12.7	0.96	0.8	0.49	6.5	1.17	2.89	5.8
PCB 105	0.380	0.39	0.027	7.05	15.7	0.06	2.6	0.03	8.0	2.77	7.58	15.2
PCB 138	4.417	4.21	0.397	9.00	12.8	0.54	4.9	0.27	6.5	4.99	10.29	20.6
PCB 156	0.171	0.17	0.016	9.48	19.8	0.03	0.4	0.02	10.1	1.23	9.55	19.1
PCB 180	0.428	0.45	0.021	4.91	15.3	0.07	4.9	0.04	7.8	4.99	6.99	14.0

Appendix A.5: Calculation and use of Z score for quality assurance

Quality Assurance of Information for the Marine Environmental Monitoring in Europe (QUASIMEME) organises internationally recognized laboratory performance studies for routine analysis of marine biota and sediment. Many laboratories take part in the laboratory studies organised by Quasimeme, making it a vital part of their quality assurance system. Individual Laboratories receive samples which they then analyse and report back to Quasimeme. The results reported are then used to calculate a |Z| score based on the values, known by QUASIMEME, present in the sample. The Z-score is calculated as follows:

Z score = mean value from laboratory - assigned value/ total error

Generated Z scores can be assessed as follows:

- $Z \leq 2$ Satisfactory performance
- $Z < 3$ Questionable performance
- $Z > 3$ Unsatisfactory performance

Appendix A.6 Preparation of PSDs for Deployment

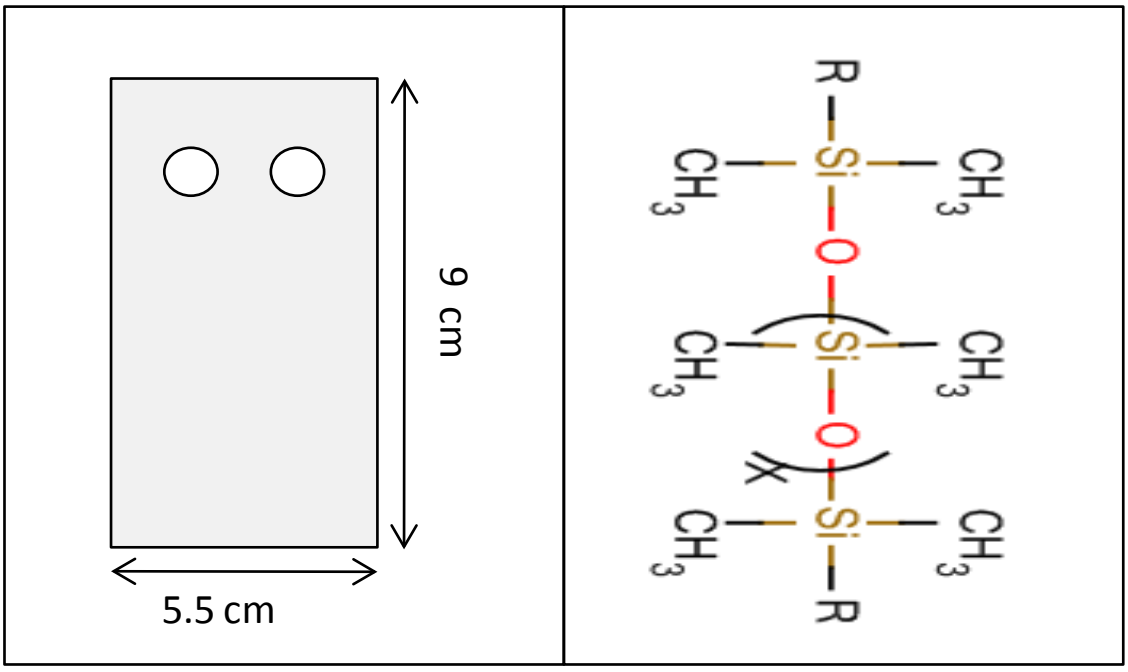
Candidate PRCs including all deuterated PAHs such as naphthalene-d_8 and phenanthrene-d_{10} plus many PCBs (*4, 10, 14, 21, 29, 30, 50, 55, 78, 104*, 112, 143, *145, 155*, 198 and *204*) not necessarily found in the environment. Spiking was performed in accordance with section A.6.2. The PRCs selected and the amount (mL) needed to spike 54 sheets for use in the Burrishoole Region are shown (*Table 4.8*) below.

Appendix A.6 Table 1 PRC compounds and concentrations used to spike 54 PDMS sheets deployed and extracted/analysed in the Burrishoole region of Co. Mayo along with molecular weight and Log K_{ow} values.

Candidate PRC	Molecular weight (g mol)	Log K_{ow}
29	257.8	5.68
30	257.8	5.62
55	292	5.88
78	292	6.28
145	360.9	6.64
155	360.9	6.54
204	466.2	7.48
Naphthalene-$_{d8}$	136.20	3.32
Ancenapththene-d_{10}	164.10	4.44
Phenanthrene-d_{10}	188.20	4.52
Chrysene-$_{d12}$	240.20	5.81
perylene-$_{d12}$	264.30	6.20
	PAH	PCB
Ideal Concentration (ng/sheet)	550 (±50)	350 (±50)
Number of Sheets	54	54
Concentration of Standards (ng/µl)	10	10
Total ng needed	29700	18900
µl of standard required	2970	1890
No of ml required (ml)	2.97	1.89

A.6.1 PDMS Devices – Description and Environmental Use

PDMS passive sampling devices were made from silicone rubber (Technirub Vizo – Netherlands) which came in a large sheet (60 cm x 60 cm x 0.5 mm). The sheets were then cut to the correct size (9 x 5.5 cm). Mounting holes were made using a 5 mm stem paper punch. (*A.6 Figure 1*) below shows the correct size and shape of the sampler. Six sheets combined together makes up one sampler with a total surface area of ~ 600 cm^2. The chemical structure of PDMS is also shown below The PDMS samplers, once they were cut to the correct size, were then extracted in a Soxhlet apparatus for at least 100 hours using ethyl acetate following a procedure optimised by Smedes *et al.* [118,89] and used in the passive sampling trial survey of 2007 which was updated in 2012.[115] This procedure removes any oligomers (short chain polymers) from the PDMS sheets. Once the extraction period was complete the sheets were immersed in methanol for 8 hours (4 mL per sheet) to remove any traces of ethyl acetate. The sheets were then ready to be spiked with PRCs.



Appendix A.6 Figure 1 (left) Shows the correct measurements needed to fabricate the PDMS sheets (right) shows the chemical structure of PDMS.

A.6.2 Spiking PDMS Sheets with PRCs

The dissipation of PRCs once the samplers are in the environment is used to calculate the effective *in situ* sampling rate (R_s). Candidate PRCs include deuterated or labelled PAHs and PCB congeners not normally found in any significant quantities in environmental matrices. The amount of PRC that was spiked to the sheets was should be chosen in such a way that allowed a residual 10 % would remaining after the samplers recovery, but also a concentration that would not exceed the calibration curve top standard after analysis. In this case the amount chosen for PAHs was 550 ng per sheet and 350 ng per sheet for PCBs.

To estimate the correct amount of PRC to add to the spiking solution simply multiply the number of sheets to be spiked by the amount chosen (550 ng for PAHs and 350 ng for PCBs). To Spike the sheets 0.6 L of methanol was added to 0.6 kg of blank PDMS sheets in a 2.5 L wide mouth flask. The spike solution was then added to the flask and shaken on an orbital shaker for 24 hours before water was added at regular periods as outlined in *A.6 Table 2.*

Appendix A.6 Table 2 Spiking procedure used to spike 0.6 kg of PDMS sheets using water and methanol.

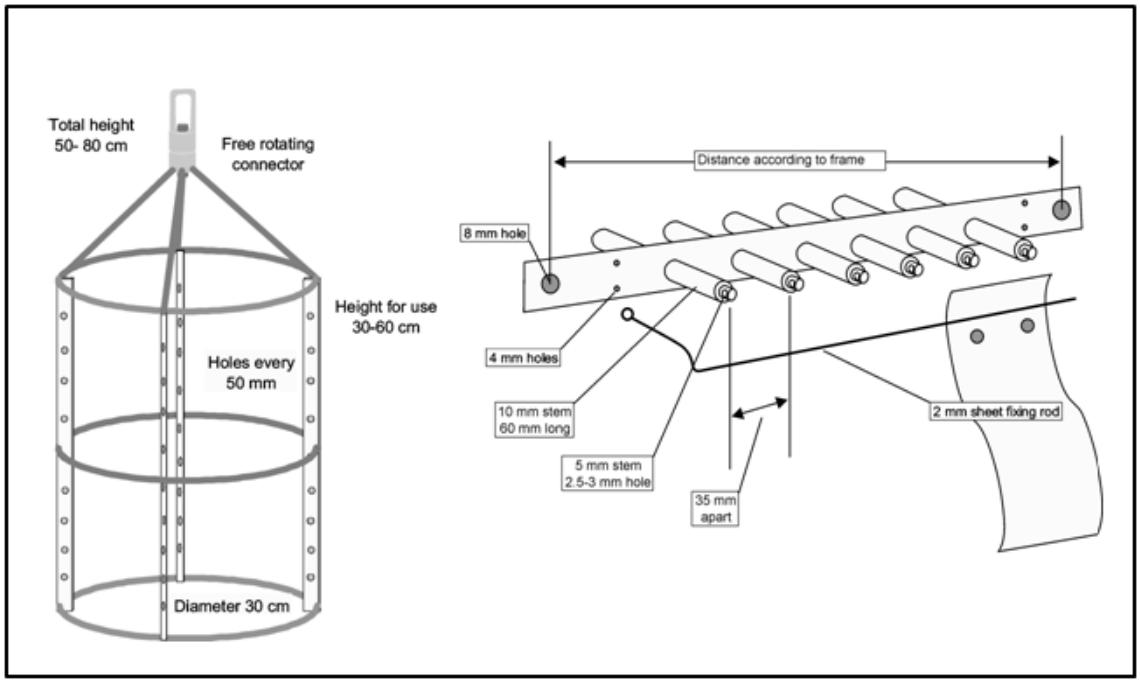
Time (h)	Volume MeOh (ml)	Added Water Volume (ml)	Total Water Volume (ml)	Water content (% v/v)
0	600	0	0	0
24	600	74	74	11
48	600	76	150	20
72+	600	107	257	30
120+	600	143	400	40
168+	600	200	600	50

The addition of water to the samplers and methanol solution forces the hydrophobic contaminants from the spiking solution into the more favourable environment of the

PDMS sampler as the percentage of water in the flask increases. Once the spiking period had finished the sheets were removed and dabbed dry using clean tissue paper before being separated into groups of six and placed in clean solvent washed jars with aluminium lined lids and then frozen (-28^{o}C). The excess water/methanol solution may still contain low levels of PRC compounds and was disposed of with care. The samplers were now ready for deployment.

A.6.3 Passive Sampler Frame

The passive sampling sheets can be fixed to the sampling frame which was fabricated from stainless steel and includes a fixing eye (free rotating connector) to give the sampler frame the flexibility to rotate. The frame can be attached to whatever object is selected in the field by affixing a rope or shackle to this fixing eye. *A.6 Figure 2* below shows the sampler cage used in this project which was a replica of the same sampler used in the ICES passive sampling trial survey.[118]



Appendix A.6 Figure 2 Passive sampler cage (left) and the sheet holder (right) used to attach PDMS passive samplers in inshore and inland Irish marine locations.

A.6.4 Deployment of Passive Samplers

Passive sampling deployment locations were selected depending on the aim of the project, but practical issues were taken into account also. If suitable mooring sites (*e.g.* jetties, tree branches or buoys) were not available then the devices were deployed using dedicated buoys at the location. Care was taken to ensure that antifouling agents or paints had not recently been applied at the location of deployment as they can interfere with the operation of the sampler. The use of excessively long ropes was avoided as it may mean that the rope could wind around other objects inhibiting recovery of the sampler. Other objects floating at the site may collide with the sampler dislodging sheets. A sampling depth of 2 meters below the surface is an appropriate depth to deploy the sampler however if the water depth was less than 3 meters then the sampler was deployed at half depth. Care was taken to ensure that at low tide the cage was still immersed in water so the site chosen should have adequate water to cover the sampler at the lowest low tide.

Exposure to air for long periods was prevented at all costs hence the sampler and any fixing ropes were readied before mounting the sampler sheets. The sheets need not be frozen right up to deployment but were transported in cooler boxes loaded with ice or ice packs. The sheets were also kept in the dark to prevent photolysis of PAH PRCs. The samplers were taken out of the cooler box at the last minute and attached to the cage without delay just before the cage was immersed in water. Field controls were exposed to the air for the same length of time as the deployed samplers to ensure that there was no uptake of contaminants prior to exposure. The sampler sheets were affixed to the cage using solvent washed tweezers. Once the sheets were all attached the fixing rod was secured in place to prevent losses of sheets. The fixing rod was then secured in

place with a cable tie. Site specific details related to individual deployments are detailed in respective chapters.

A.6.5 Recovery after Deployment

To recover the samplers they were firstly removed from the water and taken off the cage using tweezers. Depending on the level of bio-fouling the sheets were placed in the same sample jars as before the deployment if clean, or if badly bio-fouled were cleaned at the site using local water, tissues and a scourer. Regardless the sheets were dried using tissue paper before being placed back in their jars and into a cooler box for transport back to the laboratory. Field controls were again deployed for the equivalent time period that the samplers were exposed to the air to estimate any uptake of contaminants during this period. The recovery air exposure period was minimised as much as possible and the samplers were returned to laboratory and refrozen (-28^{o}C)

A.6.6 Processing of Passive Sampler Results

Preparation controls are used to give information on the spiked amounts of PRCs found in the sampler which was never deployed (N_0). The preparation control also shows the concentration of compounds taken up during the preparation of the sampler. These concentrations should be similar to the procedural blank but in some cases can be higher.

Field controls were used to identify whether elevated levels of contaminants may have been picked up by the samplers before deployment. This has been reported to be significant for PAHs in situations where samplers are deployed near factories, major

roads or if working in a plume of engine smoke when working on boats.[115] Field controls also show whether photolysis has occurred during deployment as there may be difference between certain PRCs (*e.g.* benzo(a)anthracene d-$_{12}$ or chrysene d-$_{12}$) in field and preparation controls.

Procedural blanks are used to estimate levels of contamination that may have occurred during the extraction procedures and concentrations found were used to calculate passive sampler LODs (3+SD of the blank), When extracting and analysing passive samplers it was deemed important to include a preparation and field control, a procedural blank, recovery standards and where feasible PDMS from previously characterised exposures (*e.g.* NORMAN exercise) in order to support a high degree of measurement quality control.

Appendix A.7 Burrishoole Results for all Matrices

Appendix A.7 Table 1 Upperbound PCDD/F WHO-TEQ results (pg/g w w) from eels and trout samples from the Burrishoole catchment.

		Eel	Eel	Trout
	WHO-	Furnace medium eels	Feeagh small eels	Bunevella Trout
Compound pg/g	TEQ	MSC/09/1275	MSC/09/1274	MSC/09/1273/1
Dioxins				
2,3,7,8-TetraCDD	1	0.18	0.26	3.1
1,2,3,7,8-PentaCDD	1	1.3	4.29	22
1,2,3,4,7,8-HexaCDD	0.1	0.09	0.48	1.9
1,2,3,6,7,8-HexaCDD	0.1	0.26	1.37	5.0
1,2,3,7,8,9-HexaCDD	0.1	0.09	0.45	1.6
1,2,3,4,6,7,8-HeptaCDD	0.01	0.05	0.25	0.94
OctaCDD	0.0001	0.004	0.01	0.08
Furans				
2,3,7,8-TetraCDF	0.1	0.05	0.02	0.94
1,2,3,7,8-PentaCDF	0.05	n.d	0.01	0.31
2,3,4,7,8-PentaCDF	0.5	0.27	0.38	6.3
1,2,3,4,7,8-HexaCDF	0.1	0.02	0.05	0.63
1,2,3,6,7,8-HexaCDF	0.1	0.02	0.04	0.63
1,2,3,7,8,9-HexaCDF	0.1	0.04	0.02	0.63
2,3,4,6,7,8-HexaCDF	0.1	0.04	0.04	0.63
1,2,3,4,6,7,8-HeptaCDF	0.01	0.004	0.006	0.094
1,2,3,4,7,8,9-HeptaCDF	0.01	0.004	0.003	0.094
OctaCDF	0.0001	0.0002	0.0001	0.0044
∑PCDD WHO-TEQ		1.9	7.1	34.5
∑PCDF WHO-TEQ		0.4	0.6	10.2
∑PCDD/F WHO-TEQ		2.4	7.7	45

Appendix A.7 Table 2 Concentration results calculated for all analytes included in the suite of analysis for passive samplers from Burrishoole. Also included were the PRC ratios remaining (N_t/N_0) compounds that are excluded are based on high concentrations in the T=0. Other compounds have no *Log* K_{pw} values for PSDs and are included here for reference only

Compound	Black river	Eel Wier	Bunevella	Gallaghers	T=0	LOD	Compound	Black river	Eel Wier	Bunevella	Gallaghers	T=0	LOD
PRC							HCB	1.88	0.80	0.50	0.09	0.01	0.03
Naphthalene $_{-d8}$	0.01	0.00	0.00	0.01			PCB 28	1.54	1.87	4.47	3.10	0.01	0.03
Acenaphthene $_{-d10}$	0.12	0.16	0.13	0.17			pp-DDE	4.43	4.22	5.15	2.61	0.01	0.03
Phenanthrene $-_{d10}$	0.01	0.11	0.05	0.34			PCB 149	0.43	0.64	0.17	0.31	0.15	0.45
Chrysene $-_{d12}$	0.49	0.89	0.62	0.96			PCB 118	6.49	5.33	5.43	4.55	0.19	0.57
Perylene $_{-d12}$	0.62	1.07	0.72	1.02			PCB 153	8.10	8.76	7.68	5.55	0.20	0.60
CB 29	0.86	0.93	0.80	0.91			PCB 105	3.28	1.55	2.32	1.08	0.11	0.33
CB 30	0.96	1.15	1.04	0.91			PCB 138	4.41	7.39	6.65	5.27	0.14	0.42
CB 55	0.91	0.79	0.74	0.94			PCB 180	2.93	2.38	1.59	2.58	0.09	0.27
CB 78	0.95	0.80	0.79	1.00			PCB 170	0.00	0.00	0.00	0.00	0.15	0.45
CB 145	1.01	0.83	0.82	1.00			PCB 194	2.78	2.99	2.16	2.03	0.35	1.05
CB 155	0.93	0.85	0.96	1.01			PCB 209	n.d	n.d	n.d	0.04	0.02	0.06
CB 204	1.00	1.02	1.01	0.98			A-HCH	6.33	5.54	4.50	1.25	0.02	0.07
Analytes							Aldrin	8.05	8.00	5.58	5.30	0.02	0.06
Naphthalene	36.8	37.5	28.1	34.7	0.85	2.55	B-HCH	6.62	4.08	6.06	0.01	0.01	0.04
Acenaphthylene	9.6	7.93	7.16	9.35	0.12	0.36	*Cis* -Chlordane	0.05	0.04	0.01	2.13	0.01	0.04
Acenaphthene	7.12	5.08	5.35	7.43	0.09	0.27	Dieldrin	3.74	1.48	5.50	5.90	12.3	37.0
Flourene	27.8	35.3	32.0	39.5	0.15	0.45	Edosulphane	4.69	3.07	2.85	1.40	2.52	7.55
Phenanthrene	131	178	150	105	0.40	1.20	Heptachlor	3.63	2.33	5.70	2.51	11.7	35.2
anthracene	5.02	9.8	2.30	2.75	0.10	0.30	Heptachlor epoxide	6.32	3.12	1.98	1.45	0.03	0.08
Flouranthene	115	261	162	38.9	0.21	0.63	Lindane	8.54	4.33	3.77	6.41	0.05	0.16
Pyrene	71.1	153	105	27.3	0.12	0.36	op-DDD	0.26	0.00	0.00	0.00	0.01	0.03
Chrysene	9.6	23.0	20.9	3.24	0.15	0.45	op-DDT	17.2	18.3	10.7	5.02	0.01	0.04
Benzo(a)anthracene	27.8	91.8	60.9	9.9	0.13	0.39	Oxychlordane	6.39	0.01	3.36	1.87	1.62	4.87
Benzo(b)flouranthene	11.5	62.3	31.3	3.17	0.11	0.33	ppDDD	0.02	0.05	0.05	0.04	0.04	0.12
Benzo(k)flouranthene	10.3	41.1	22.1	2.75	0.09	0.27	pp-DDT	14.3	15.4	5.10	0.93	0.01	0.02
Benzo(a)pyrene	4.54	9.37	6.59	1.74	0.09	0.27	*Trans* -Chlordane	2.57	0.80	1.90	0.93	0.01	0.03
Indeno(1,2,3-cd)pyrene	7.28	16.3	8.82	2.32	0.11	0.33	*Trans*- nonachlor	1.94	1.34	1.32	0.29	0.01	0.03
Dibenzo(a,h)anthracene	4.78	5.47	3.03	1.33	0.16	0.48							
Benzo(g,h,i)perylene	5.02	10.7	6.48	2.36	0.14	0.42							

Appendix A.7 Table 3 Summary table containing all PCB data obtained from analysis of Passive samplers (ng/L), sediment (ng/g d w) and biota (ng/g w w)

Location	L Feeagh	Furnace	Bunevella	Eel Wier	Black river	Bunevella	Cork	Dublin	Bantry	Omey Island	Gallaghers	Black River	Eel weir	Bunevella	Gallaghers
Sample Number	MSC/09/1274	MSC/09/1273	MSC/09/1275	PDMS 13 -001	PDMS 13 -002	PDMS 13 -003	PDMS 13 -005	PDMS 13 -006	PDMS 13 -007	PDMS 13 -008	PDMS 13 -004				
Matrix	Eel	Trout	Eel	PSD	PSD	PSD	PSD	PSD	PSD	PSD	PSD	Sediment	Sediment	Sediment	Sediment
Code	LF1(Eel)	FU(Tr)	LF2(Eel)	EW(PDMS)	BR(PDMS)	BU(PDMS)	CK(PDMS)	DU(PDMS)	BY(PDMS)	OI(PDMS)	GL(PDMS)				
$\sum PCB_7$															
PCB 28	43.8	18.4	15.7	0.10	0.02	0.24					0.29				0.03
PCB 52	155	48.8	42.7												0.06
PCB 118	375	291	244	0.31	0.08	0.32	0.15	0.22	0.01	0.04	0.47				0.11
PCB 101	224	81.7	69.4				0.02	0.02	0.004	0.02					0.09
PCB 138	940	440	370	0.45	0.06	0.41	0.15	0.14	0.01	0.01	0.57				0.12
PCB 153	1,940	755	657	0.54	0.11	0.47	0.14	0.26	0.02	0.02	0.60				0.15
PCB 180	659	220	179	0.15	0.04	0.10	0.12	0.23	0.01	0.00	0.29				0.09
PCB 31															0.02
PCB 44							0.01	0.01	0.01	0.05					0.05
PCB 77	1.01	0.63	0.54												
PCB 81	0.20	0.13	0.11												
PCB 105	94.4	72.8	61.1	0.09	0.04	0.14					0.11				0.01
PCB 114	3.57	3.45	3.09												
PCB 123	4.76	4.26	2.82												
PCB 126	4.84	0.54	0.47												
PCB 149				0.04	0.01	0.01	0.10	0.09	0.0004	0.02	0.03				0.00
PCB 156	42.6	40.2	33.7				0.07	0.02	0.00004	0.01	0.00				0.02
PCB 157	12.3	8.51	7.15												
PCB 167	46.1	20.5	16.3												
PCB 169	1.39	0.63	0.54												
PCB 170							0.02	0.01	0.003	0.004					
PCB 189	13.0	3.19	2.59												
PCB 209							0.01	0.04	0.01	0.01					

Appendix A.7 Table 4 Summary table containing all PAH and OC data obtained from analysis of Passive samplers (ng/L), sediment (ng/g d w) and biota (ng/g w w)

Location	Eel Wier	Black river	Bunevella	Cork	Dublin	Bantry	Omey Island	Gallaghers	Black River	Eel weir	Bunevella	Gallaghers
Sample Number	PDMS 13 -001	PDMS 13 -002	PDMS 13 -003	PDMS 13 -005	PDMS 13 -006	PDMS 13 -007	PDMS 13 -008	PDMS 13 -004				
Matrix	PSD	PSD	PSD	PSD	PSD	PSD	PSD	PSD	Sediment	Sediment	Sediment	Sediment
Code	EW(PDMS)	BR(PDMS)	BU(PDMS)	CK(PDMS)	DU(PDMS)	BY(PDMS)	OI(PDMS)	GL(PDMS)				
Acenaphthylene	4.36	5.28	3.93	1.11	3.24	1.36	0.30	5.14	12.5	2.00	11.4	12.9
Acenaphthene	1.22	1.71	1.29	2.02	2.64	0.57	0.14	1.85	2.00	1.70	2.00	1.90
Fluorene	5.86	4.51	5.30	5.32	4.12	2.85	0.67	7.26	1.50	1.50	1.90	1.20
Phenanthrene	16.6	10.2	14.1	9.48	4.85	2.88	1.27	13.0	22.7	5.50	30.2	29.2
anthracene	0.80	0.31	0.19	0.48	0.89	0.16	0.05	0.31	3.30	5.40	4.00	3.40
Fluoranthene	15.6	3.06	9.6	5.60	5.47	0.66	0.52	3.72	48.4	3.80	95.9	82.8
Pyrene	8.84	1.71	6.05	3.39	6.10	0.26	0.10	2.56	35.1	5.40	66.3	50.3
Chrysene	1.23	0.14	1.12	0.47	1.09	0.01	0.02	0.30	16.3	1.00	36.7	33.5
Benzo(a)anthracene	4.86	0.38	3.23	1.17	1.64	0.05	0.04	0.92	37.5	1.90	124	61.9
Benzo(b)fluoranthene	3.28	0.14	1.65	0.76	0.89	0.02	0.02	0.29	70.2	3.10	171	85.2
Benzo(k)fluoranthene	2.16	0.13	1.16	0.76	0.54	0.02	0.02	0.26	35.8	0.90	58.8	30.4
Benzo(a)pyrene	0.49	0.06	0.35	0.28	0.67	0.005	0.01	0.16	31.6	2.30	41.1	29.7
Indeno(1,2,3-cd)pyrene	0.89	0.09	0.48	0.47	0.19	0.01	0.01	0.22	31.5	1.10	83.4	34.8
Dibenzo(a,h)anthracene	0.30	0.06	0.16	0.11	0.07	0.001	0.003	0.13	8.30	0.20	24.1	9.7
Benzo(g,h,i)perylene	0.58	0.06	0.35	0.39	0.24	0.003	0.004	0.23	19.7	1.20	47.8	26.6
α-HCH	2.91	3.32	2.36					0.66				
β-HCH	2.09	3.40	3.11					0.01				
op-DDT	0.94	0.20	0.31	0.02	0.02	0.95	0.02	0.10				
pp-DDT	0.09	0.20	0.13	0.02	0.44	0.12	0.29	0.11				
pp-DDE	0.24	0.06	0.30	0.08	0.04	0.00	0.10	0.27				
op-DDD				3.22	3.47	0.32	0.28					
pp-DDD				5.99	0.84	0.19	0.73					
trans -chlordane	0.22	0.04	0.14					0.17				
Heptachlor epoxide	0.10	0.14	0.36					0.68				
endosulphane				2.58	0.01	2.24	0.01					
HCB	0.05	0.03	0.03	0.08	0.11	0.00	0.01	0.01				
PAH profiles												
P/A	20.9	32.8	74.8	19.7	5.43	17.6	23.5	41.6	6.88	1.02	7.55	8.59
Fl/Py	1.76	1.79	1.59	1.65	0.90	2.52	5.12	1.45	1.38	0.70	1.45	1.65
∑L-PAHs/∑H-PAHs	0.76	3.77	1.02	1.38	0.93	7.52	3.27	3.13	0.13	0.77	0.07	0.11

Appendix A.7 Table 5 Concentrations of PCDD in biota (pg/g wet weight), in PDMS passive samplers (pg/g sampler), sediment (ng/g d w). Total PCP/PCA as ng PCP in sediment g d w and biota per g w w. Sum 7 marker PCBs in biota (ng/g wet weight) and sediment (ng/g d w). Also included are the data from Sundquist *et al.* [66] used in the generation of PCA plot (*fig 4.10*).

	R. Suir	L. Conn	R Corrib	R Fane	Ky-5(ca 805 Teq)	Sevarex tech mix(47)	Witophen N (100 %)	Sevarex Granulate	Santobite D (100 %)	Schering-Plough	Novartis	Schering-Plough	Smithkline Beecham	Eli-Lily	Finsa Forest Product
	Conc	Conc	Conc	Conc	Rel to 1	Rel to 2	Rel to 3	Rel to 4	Rel to 5	Conc	Conc	Conc	Conc	Conc	Conc
MSC Number	MSC/05/1119	MSC/05/1120	MSC/05/1121	MSC/05/1122											
Sampling year	2005	2005	2005	2005						2011	2010 -12	2010 -12	2010 -12	2010 -12	2010
Matrix	Eel	Eel	Eel	Eel	Tech Mix	Tech Mix	Tech Mix	Tech Mix	Tech Mix	Emission	Emission	Emission	Emission	Emission	Emission
Code	RS(eel)	LC(eel)	RC(eel)	FR(eel)	KY5(TM)	SEV(TM)	WIT(TM)	SEVG(TM)	SAN(TM)	RA(EM)	CK(EM1)	WK(EM)	CK(EM2)	CK(EM3)	SC(EM)
2378TF	0.01	0.01	0.01	0.01	0.0002	0.000004	0.0001	0.000006	0.000006	0.06	0.005	0.01	0.01	0.01	0.01
12378PeF	0.02	0.01	0.02	0.02	0.001	0.000004	0.0008	0.00009	0.00003	0.08	0.002	0.04	0.01	0.01	0.04
23478PeF	0.15	0.10	0.06	0.09	0.002	0.000008	0.0006	0.00001	0.00001	0.1	0.004	0.02	0.01	0.01	0.04
123478HxF	0.05	0.06	0.03	0.06	0.007	0.001	0.004	0.0007	0.0006	0.1	0.01	0.02	0.01	0.01	0.03
123678HxF	0.03	0.04	0.02	0.03	0.003	0.0001	0.001	0.0001	0.0001	0.1	0.004	0.02	0.01	0.01	0.03
123789HxF	0.01	0.01	0.01	0.01	0.003	0.00004	0.002	0.0001	0.0008	0.01	0.006	0.004	0.01	0.01	0.01
234678HxF	0.09	0.09	0.08	0.07	0.21	0.0003	0.007	0.0005	0.0006	0.1	0.007	0.02	0.02	0.01	0.03
1234678HpF	0.04	0.01	0.01	0.01	0.26	0.02	0.2	0.02	0.05	0.23	0.01	0.04	0.05	0.03	0.70
1234789HpF	0.01	0.01	0.01	0.01	0.002	0.003	0.001	0.00	0.005	0.01	0.005	0.07	0.01	0.01	0.02
OCDF	0.01	0.01	0.01	0.01	0.040	0.1	0.06	0.10	0.2	0.04	0.03	0.02	0.02	0.03	0.82
2378TD	0.04	0.03	0.02	0.03		0.000005		0.00001	0.002	0.003	0.004	0.01	0.003	0.01	0.003
12378PeD	0.10	0.08	0.09	0.09				0.00001		0.01	0.002		0.004	0.01	0.003
123478HxD	0.03	0.08	0.04	0.06	0.004	0.008	0.005	0.02	0.01	0.01	0.003	0.003	0.003	0.004	0.01
123678HxD	0.16	0.17	0.10	0.23						0.02	0.04	0.01	0.01	0.01	0.17
123789HxD	0.04	0.04	0.01	0.03	0.001	0.001	0.001	0.001	0.0004	0.01	0.004		0.004	0.01	0.06
1234678HpD	0.11	0.11	0.05	0.08	0.01	0.1	0.01	0.2	0.1	0.06	0.02	0.02	0.04	0.03	3.20
OCDD	0.01	0.01	0.01	0.01	0.004	0.4	0.02	0.4	0.3	0.08	0.05	0.04	0.07	0.06	5.47
∑PCDD	0.50	0.52	0.32	0.52											
∑PCDF	0.43	0.34	0.26	0.32											
∑PCDD/F	0.92	0.86	0.58	0.84											
∑PCB_7	18.1	3.63	1.94	7.64											
DL-PCBs	4.36	0.92	0.48	2.31											
PCDF(%)	38.7	33.3	37.4	34.5											
PCDD(%)	61.3	66.7	62.6	65.5											
PCP/PCA	0.00	1.12	1.54	0.00											
HCB	0.50	1.00	0.80	0.90											

Appendix A.8 M6 Deployment Data

Appendix A.8 Table 1 SPMD and PDMS concentrations (ng sampler) of PAHs in sampler deployed at the M6 weather buoy. Also included are the recoveries of PRCs (N_t/N_0) in PDMS passive samplers.

	250 m		750 m		1040 m				PDMS PSD					
Compound (ng sampler)	**SPMD 1**	**SPMD 2**	**SPMD 1**	**SPMD 2**	**SPMD 1**	**SPMD 2**	**LOD**	**T_0**	**5 m**	**250 m**	**750 m**	**1040 m**	**LOD**	**T_0**
Naphthalene	14.4	15.9	15.7	16.1	16.3	15.5	2.85	3.85	116	36.9	49.9	30.1	4.15	6.59
Acenaphthylene	1.21	1.56	1.32	0.93	1.12	1.28	0.16	0.21	2.15	0.32	0.25	0.17	0.01	0.04
Acenaphthene	1.11	1.17	0.85	0.76	0.75	0.61	0.18	0.20	5.61	1.01	0.56	0.47	0.04	0.15
Fluorene	4.32	4.58	3.73	3.73	3.21	3.09	0.44	0.49	9.9	4.03	2.22	2.16	0.15	0.33
Phenanthrene	14.7	15.3	14.5	13.8	11.4	12.2	0.32	0.79	168	127	135	86.8	1.02	1.47
Anthracene	1.07	1.21	1.13	1.08	0.95	1.07	0.11	0.18	5.30	8.60	10.0	5.69	0.10	0.22
Fluoranthene	7.15	7.13	28.8	27.9	21.1	26.7	0.54	0.81	52.0	50.0	128	105	1.12	1.29
Pyrene	2.08	1.94	5.46	5.36	4.43	5.79	0.68	0.74	21.5	9.45	16.6	13.3	1.01	1.08
Benz[a]anthracene	9.9	9.32	22.7	22.2	17.6	24.3	0.79	1.01	32.1	35.6	70.2	49.9	1.08	1.24
Chrysene	1.40	1.38	1.49	1.50	1.15	1.33	0.25	0.28	8.27	4.15	3.68	2.31	0.79	0.84
Benzo[b]fluoranthene	5.32	4.92	7.95	5.94	7.81	11.4	0.50	0.81	42.6	49.8	68.5	23.8	1.12	1.60
Benzo[k]fluoranthene	7.12	6.75	8.29	6.62	7.79	9.24	0.30	0.48	32.7	38.1	55.6	23.3	1.23	1.27
Benzo[a]pyrene	1.35	1.17	1.11	1.11	0.98	1.14	0.22	0.28	66.0	22.7	0.93	15.2	0.15	0.24
Indeno[1,2,3-cd]pyrene	0.53	0.25	0.55	0.19	0.82	1.60	0.02	0.02	11.3	2.87	0.56	2.65	0.12	0.30
Dibenzo[a,h]anthracene	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.05	0.06	1.51	<0.015	<0.015	<0.015	0.15	0.26
Benzo(g,h,i)perylene	0.30	<0.01	0.31	0.17	<0.01	0.29	0.01	0.02	8.30	5.96	7.17	2.05	0.18	0.22
$\sum PAH_{14}$	71.9	72.6	114	107	95.4	115			583	397	549	363		
N_t/N_0	**5M**	**250M**	**750M**	**1040 M**										
Naphthalene-$_{d8}$	0.00	0.00	0.00	0.00										
Ancenapththene-$_{d10}$	0.00	0.00	0.00	0.00										
Phenanthrene-$_{d10}$	0.00	0.00	0.00	0.00										
Chrysene-$_{d12}$	0.00	0.06	0.00	0.00										
Perylene-$_{d12}$	0.00	0.11	0.82	0.02										
PCB 29	0.00	0.04	0.16	0.04										
PCB 30	0.02	0.01	0.04	0.02										
PCB 55	0.11	0.01	0.03	0.20										
PCB 78	0.19	0.29	0.07	0.27										
PCB 145	0.38	0.54	0.17	0.54										
PCB 155	0.48	0.61	0.35	0.57										
PCB 204	0.46	0.65	0.44	0.55										

Appendix A.8 Table 2 SPMD and PDMS concentrations of PCBs (ng sampler) found in the returned M6 weather buoy samples.

	250 m		750 m		1040 m				PDMS PSD					
Compound (ng sampler)	**SPMD 1**	**SPMD 2**	**SPMD 1**	**SPMD 2**	**SPMD 1**	**SPMD 2**	**LOD**	**T_0**	**5 m**	**250 m**	**750 m**	**1040 m**	**LOD**	**T_0**
PCB 18	<0.21	<0.21	0.35	0.39	0.50	0.37	0.21	0.12	2.10	1.84	4.87	0.48	0.05	0.11
PCB 28	0.47	0.41	0.79	1.23	0.44	0.67	0.01	0.02	3.97	3.41	6.19	0.76	0.08	0.12
PCB 31	0.65	0.57	0.34	0.37	0.44	0.38	0.07	0.07	3.97	3.86	6.08	0.83	0.01	0.02
PCB 44	0.72	0.66	0.92	1.23	0.22	0.12	0.01	0.02	2.63	4.27	17.5	0.89	0.01	0.04
PCB 52	0.73	0.79	1.23	1.22	0.67	0.59	0.01	0.03	1.61	3.79	17.6	1.48	0.01	0.16
PCB 101	1.12	1.06	1.89	1.43	1.52	1.32	0.01	0.04	3.09	7.81	17.4	1.78	0.01	0.08
PCB 149	1.10	0.93	3.03	3.51	1.43	3.85	0.01	0.06	2.31	4.52	18.5	1.34	0.01	0.10
PCB 105	0.59	0.62	1.73	1.90	0.23	0.17	0.01	0.02	4.73	3.40	8.53	1.70	0.02	0.25
PCB 118	1.76	1.66	4.25	4.80	1.58	1.52	0.01	0.05	4.44	9.9	17.2	3.04	0.02	0.18
PCB 138	1.23	1.18	2.99	3.41	1.84	1.54	0.004	0.08	6.66	16.3	43.0	0.98	0.02	0.23
PCB 153	1.71	1.76	3.54	3.73	3.34	3.55	0.01	0.06	11.4	9.41	16.3	2.07	0.02	0.16
PCB 156	0.18	0.21	0.35	0.84	0.08	0.06	0.004	0.004	0.32	1.97	19.0	0.26	0.01	0.18
PCB 170	0.10	0.11	0.20	0.22	0.13	0.10	0.01	0.02	2.17	2.28	6.47	17.6	0.01	0.08
PCB 180	0.21	0.21	0.52	0.56	0.43	0.46	0.01	0.02	0.52	1.58	1.03	0.47	0.16	0.17
PCB 194	0.63	0.64	<0.01	<0.01	<0.01	0.01	0.01	0.01	<0.02	2.73	1.53	0.55	0.02	0.02
PCB 209	0.02	<0.01	<0.01	0.02	0.07	<0.01	0.01	0.01	0.05	4.85	10.0	0.23	0.02	0.02
∑PCB	11.2	10.8	22.1	24.8	12.9	14.7			50.0	81.9	211	34.5		

Appendix A.8 Table 3 SPMD and PDMS concentrations of OCs (ng sampler) found in the returned M6 weather buoy samples.

	250 m		750 m		1040 m				PDMS PSD					
Compound (ng sampler)	**SPMD 1**	**SPMD 2**	**SPMD 1**	**SPMD 2**	**SPMD 1**	**SPMD 2**	**LOD**	**T_0**	**5 m**	**250 m**	**750 m**	**1040 m**	**LOD**	**T_0**
HCB	9.08	9.24	12.1	14.5	10.0	11.6	0.22	0.56	0.50	0.87	1.13	3.03	0.02	0.06
α-HCH	0.76	0.81	1.07	1.34	0.86	0.82	0.02	0.12	8.74	6.37	5.44	4.42	0.02	0.18
γ-HCH	0.57	0.58	0.37	0.19	0.53	1.20	0.01	0.09	23.2	19.1	4.38	2.17	0.01	3.21
β-HCH	<0.01	0.02	0.52	0.30	0.22	0.58	0.01	0.06	16.7	16.5	10.8	9.33	0.02	0.18
Heptachlor	0.21	0.23	0.26	0.74	0.16	0.86	0.01	0.04	25.6	15.5	13.7	13.9	0.18	0.26
Oxychlordane	10.1	10.2	5.79	17.1	36.1	17.5	0.02	0.21	1.25	5.28	7.31	6.62	0.11	0.18
Heptachlor Epoxide	0.89	0.68	0.50	0.70	0.38	0.30	0.02	0.03	12.7	3.74	4.26	6.60	0.22	0.35
trans-Chlordane	0.38	0.47	0.70	0.82	0.53	0.98	0.03	0.06	<0.25	<0.25	<0.25	<0.25	0.25	<0.025
trans-Nonachlor	1.59	1.67	1.04	1.16	15.0	15.6	0.14	0.26	<0.16	<0.16	13.9	1.57	0.16	1.21
o,p'-DDE	0.18	0.27	2.04	2.64	2.33	1.42	0.02	0.03	11.5	6.19	4.52	5.62	0.01	0.33
cis-Chlordane	0.58	0.69	1.89	2.03	0.98	1.10	0.20	0.22	2.15	3.74	2.90	0.89	0.01	0.30
Endosulfan	0.51	0.52	0.59	0.81	0.52	0.56	0.01	0.12	17.2	8.50	11.9	7.05	1.58	5.26
p,p'-DDE	2.53	2.47	11.7	13.5	13.8	13.8	0.09	0.59	1.74	3.64	12.6	6.14	0.01	0.17
Dieldrin	0.54	0.51	3.68	8.72	5.84	3.21	0.01	0.06	11.9	7.78	13.6	6.59	0.02	0.36
o,p'-DDD	0.10	0.13	1.54	1.43	0.83	0.71	0.02	0.04	0.35	0.21	1.79	<0.02	0.02	0.03
Endrin	1.19	1.29	1.84	1.95	1.14	1.47	0.03	0.13	0.35	0.21	1.79	<0.02	0.02	0.68
o,p'-DDT	0.83	1.18	2.35	3.22	2.28	2.75	0.12	0.16	<0.01	7.41	2.30	<0.02	0.01	0.10
p,p'-DDD	0.33	0.33	1.95	2.36	0.79	0.88	0.02	0.04	41.5	24.1	11.7	11.4	0.02	0.35
p,p'-DDT	0.89	0.94	3.37	4.29	3.02	3.80	0.40	0.06	38.9	9.7	30.0	77.5	0.02	0.44
∑OCPs	31.3	32.2	53.3	77.8	95.2	79.1			214	139	154	163		

Appendix A.8 Table 4 Flow meter measurements made across the length of the deployment of PSDs at M6 and average CTD measurements of temperature and salinity made at the M6 weather buoy in Feburary 2010 by McGrath *et al.* [178]

5M			**250M**			**500M**		
sector (deg)	**frequency (%)**	**mean speed (m/s)**	**sector (deg)**	**frequency (%)**	**mean speed (m/s)**	**sector (deg)**	**frequency (%)**	**mean speed (m/s)**
0	2.92	0.15	0	4.15	0.11	0	4.38	0.11
30	5.34	0.20	30	8.68	0.15	30	8.37	0.14
60	11.0	0.25	60	10.7	0.20	60	9.07	0.19
90	15.4	0.26	90	15.4	0.22	90	14.1	0.21
120	16.1	0.26	120	18.6	0.21	120	18.4	0.19
150	17.4	0.25	150	14.2	0.20	150	14.8	0.19
180	12.0	0.26	180	13.3	0.22	180	13.9	0.21
210	8.24	0.22	210	8.86	0.19	210	10.5	0.17
240	4.51	0.16	240	2.41	0.11	240	2.49	0.10
270	2.41	0.13	270	1.11	0.08	270	1.06	0.07
300	2.17	0.13	300	1.09	0.07	300	1.04	0.06
750M			**1040M**			Average temperature and salinity measurments		
sector (deg)	**frequency (%)**	**mean speed(m/s)**	**sector(deg)**	**frequency(%)**	**mean speed (m/s)**	**Depth**	**average temp**	**Average salinity**
0	5.04	0.10	0	5.35	0.09			
30	6.45	0.11	30	3.50	0.10	0 -20 m	10.96	35.48
60	7.38	0.14	60	5.81	0.10	20 - 400 m	10.80	35.44
90	11.8	0.15	90	8.42	0.10	400 - 500 m	9.75	35.28
120	16.1	0.15	120	13.8	0.11	500 - 600 m	8.81	35.19
150	17.4	0.15	150	18.3	0.12	600 - 700 m	7.21	35.03
180	17.1	0.17	180	20.3	0.15	700 - 800 m	7.81	35.30
210	12.0	0.14	210	13.9	0.13	800 - 900 m	5.89	35.04
240	2.68	0.07	240	3.78	0.08	900 - 1000 m	5.58	35.05
270	1.13	0.05	270	2.15	0.05	1000 - 1100 m	4.98	34.99
300	1.13	0.05	300	1.96	0.05			

Appendix A.9 Chapter 6 Data

Appendix A.9 Table 1 Results (ng/ sampler) for all passive samplers for WFD and non-WFD sites from across Ireland

Location	Mutton Island	Dublin Port	Bantry Bay	Omey Island	Cork 1	Cork 2	Wexford Harbour	Shannon	T=0	LOD	NWA Seaboard	Gweebarra Bay	Erne Estuary	Furnace Lough	Kilkeiran	Lower Shannon	Upper Shannon	Limerick Dock	Upper Blackwater	upper Suir	New Ross	upper Barrow	Nore Estuary	Upper Slaney	T=0	LOD
Latitude	53.259257°N	53.345223°N	51.641885°N	53.528677°N	51.837793°N	51.837793°N	52.339849°N	52.689806°N			54.86877°N	54.84115°N	54.50612°N	53.90069°N	53.31804°N	52.63312°N	52.68114°N	52.65645°N	52.14925°N	52.32735°N	52.36772°N	52.4881°N	52.48555°N	52.45274°N		
Longitude	9.041061°W	6.214314°W	9.699554°W	10.168533°W	8.29073°W	8.29073°W	6.457729°W	8.903046°W			8.53792°W	8.4627°W	8.22073°W	9.57333°W	9.72797°W	9.1223°W	8.82172°W	8.66077°W	7.85817°W	7.31669°W	6.9661°W	6.932°W	7.06479°W	6.52999°W		
year	2010	2010	2010	2010	2010	2010	2010	2010			2012	2012	2012	2012	2012	2012	2012	2012	2012	2012	2012	2012	2012	2012		
Device type	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS			PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS	PDMS		
Water Body type	Saline	Saline	Saline	Saline	Saline	Saline	Saline	Saline			Saline	Saline	Fresh	Mixed	Saline	Mixed	Mixed	Fresh	Fresh	Fresh	Fresh	Fresh	Fresh	Fresh		
Site description	Marine	Estuary	Marine	Marine	Estuary	Estuary	Estuary	Estuary			Marine	Marine	Estuary	River	Marine	Estuary	Estuary	Estuary	Estuary	River	River	River	Estuary	River		
Compound ng/sampler																										
Naphthalene	8.00	11.2	64.9	8.40	5.28	10.1	5.26	18.8	1.03	3.09	8.13	7.83	19.3	6.01	12.7	14.5	15.1	11.2	38.7	28.6	31.8	15.2	25.2	3.60	7.39	22.2
Acenaphthylene	2.48	10.5	4.39	0.99	3.58	2.76	5.51	5.21	0.46	1.38	0.31	9.07	1.21	1.96	0.51	8.72	18.2	8.34	1.54	30.6	6.37	1.46	2.79	1.57	0.02	0.05
Acenaphthene	2.43	19.6	4.26	1.03	15.0	10.1	32.0	8.42	0.19	0.58	0.22	3.89	0.74	3.20	0.34	27.6	46.0	33.5	5.61	27.1	7.72	2.54	3.50	3.54	0.03	0.10
Fluorene	10.0	45.2	31.3	7.32	58.1	42.6	34.2	49.4	0.42	1.26	0.83	1.15	1.86	7.75	0.40	37.0	39.9	15.9	5.62	80.5	13.9	16.9	6.20	3.03	0.01	0.04
Phenanthrene	47.6	110	66.0	29.1	201	183	107	285	0.66	1.98	48.8	91.9	222	69.5	130	143	171	139	209	256	206	218	248	84.6	0.03	0.08
anthracene	4.69	24.9	4.72	1.54	12.1	15.8	36.2	20.1	0.39	1.17	29.5	17.4	93.2	3.08	6.74	34.6	31.1	6.59	7.96	46.4	57.7	30.8	55.7	69.1	0.01	0.04
Fluoranthene	74.5	291	49.3	30.6	219	195	397	440	0.44	1.31	36.1	47.6	232	78.7	135	196	217	247	169	282	202	264	190	116	0.01	0.04
Pyrene	46.3	346	22.4	6.45	138	125	274	288	0.73	2.18	13.3	30.4	163	53.6	68.4	211	214	195	109	215	192	172	146	166	0.00	0.01
Chrysene	10.4	82.3	3.42	1.68	22.1	19.6	138	38.3	0.55	1.65	1.36	3.23	28.3	7.38	9.6	38.5	52.5	52.7	16.2	59.3	82.5	55.5	20.3	1.92	0.01	0.03
Benzo(a)anthracene	23.1	126	15.2	3.58	55.9	50.9	278	127	0.22	0.66	5.45	13.6	50.3	13.1	21.0	37.2	44.3	57.0	23.2	62.2	70.8	42.0	30.8	2.84	0.01	0.03
Benzo(b)fluoranthene	9.45	72.2	8.11	1.66	37.0	32.9	206	31.9	0.52	1.56	2.29	1.47	8.25	2.89	3.03	9.44	14.0	12.5	3.27	15.5	29.0	6.74	4.51	0.43	0.00	0.01
Benzo(k)fluoranthene	6.27	43.3	9.40	1.86	37.0	31.1	180	31.9	0.61	1.83	0.78	1.75	13.0	4.49	5.12	17.4	22.6	19.1	4.26	22.2	38.5	11.0	12.5	0.68	0.01	0.02
Benzo(a)pyrene	5.46	54.2	2.23	1.22	13.4	10.8	43.9	9.8	0.28	0.84	0.57	1.91	6.60	4.93	2.38	8.87	12.6	13.6	2.02	15.1	24.2	4.17	4.87	0.45	0.01	0.03
Indeno(1,2,3-cd)pyrene	3.27	15.2	3.11	0.71	22.4	14.7	42.4	8.15	0.22	0.66	0.68	0.60	6.55	2.02	1.41	4.35	6.38	6.91	2.39	9.17	15.0	5.72	4.05	3.65	0.02	0.05
Dibenzo(a,h)anthracene	1.58	5.93	0.59	0.27	5.18	2.25	8.96	0.89	0.08	0.24	0.10	0.11	0.68	0.32	0.03	1.06	1.33	0.52	1.77	0.78	1.30	0.64	0.77	0.70	0.02	0.07
Benzo(g,h,i)perylene	2.78	19.3	1.76	0.41	18.2	12.9	34.1	7.90	0.12	0.36	0.41	0.58	10.1	2.42	1.81	6.92	8.11	9.05	2.70	9.6	17.5	4.03	2.65	4.85	0.02	0.05
PCB 18	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*		1.52	3.03	1.77	n.d*	0.27	4.67	29.8	23.6	2.77	23.6	27.0	11.1	20.6	5.81	0.01	0.04
PCB 31	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.01	0.04	1.93	2.51	2.10	2.38	0.21	1.48	4.13	7.71	0.91	1.94	4.57	0.74	1.51	0.55	0.01	0.03
PCB 28	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.06	0.17	4.35	1.68	4.97	1.17	0.34	3.02	4.02	8.91	2.61	4.73	8.75	3.80	2.62	2.01	0.01	0.04
PCB 52	n.d*	n.d*	n.d*	n.d*	7.68	7.83	n.d*	8.91	n.d*		0.89	0.58	0.75	1.58	0.18	2.30	5.72	6.89	1.58	2.48	6.54	0.95	1.38	1.06	0.01	0.03
PCB 44	n.d	n.d	n.d	n.d	3.36	3.18	n.d	10.5	0.01	0.03	0.73	1.45	3.01	0.56	0.10	1.99	3.64	5.15	1.46	2.01	4.87	0.72	1.01	1.64	0.01	0.03
PCB 101	n.d	n.d	2.05	n.d	5.66	5.12	n.d	n.d	n.d		1.16	1.76	1.22	0.41	0.13	3.23	5.91	5.08	1.03	1.53	5.08	0.70	0.57	0.51	0.01	0.02
PCB 149	0.92	6.71	0.02	0.72	4.16	4.66	25.8	0.00	0.01	0.03	0.58	0.29	0.64	0.32	0.07	1.73	2.66	1.66	0.42	3.57	3.61	0.13	0.72	0.24	0.01	0.02
PCB 118	6.58	15.9	7.29	7.71	6.52	5.08	6.71	6.58	0.01	0.03	1.09	2.29	0.47	0.23	0.44	2.03	4.20	2.34	0.34	2.78	6.25	0.92	1.70	0.68	0.01	0.03
PCB 153	12.3	18.5	9.25	12.9	5.95	6.44	7.73	11.5	0.01	0.02	0.79	7.30	4.86	1.40	0.92	2.78	4.09	3.18	0.58	3.31	3.32	1.11	1.52	0.77	0.02	0.05
PCB 105	2.17	3.28	0.70	13.3	0.15	0.15	17.3	n.d	0.05	0.14	3.99	3.59	1.66	2.44	0.85	3.87	5.74	6.20	1.36	1.73	2.61	2.16	1.95	2.67	1.99	5.96
PCB 138	6.61	9.9	5.76	9.9	6.38	6.04	7.38	11.9	0.06	0.17	0.27	2.85	0.80	0.39	0.25	2.62	2.93	1.61	0.28	0.80	1.72	0.39	0.66	0.16	0.003	0.01
PCB 156	0.56	1.11	0.02	1.10	2.91	5.71	10.9	30.0	0.02	0.06	0.30	0.65	0.27	1.14	0.04	0.72	0.29	0.19	0.03	0.12	0.11	0.07	0.08	0.02	0.004	0.01
PCB 180	2.51	15.3	2.87	1.99	4.76	4.97	6.10	4.41	0.03	0.08	0.68	0.32	0.43	0.42	0.10	1.59	1.36	0.93	0.06	0.59	0.75	0.18	0.43	0.17	0.01	0.03
PCB 170	n.d	0.84	1.70	0.25	0.85	1.54	11.4	1.10	0.02	0.07	0.07	0.04	0.01	0.08	0.01	0.15	0.26	0.11	0.06	0.14	0.14	n.d	0.01	n.d	0.003	0.01
PCB 194	0.35	4.05	1.58	0.23	n.d	n.d*	n.d	29.1	0.04	0.11	n.d	0.30	n.d	n.d	0.003	n.d	0.11	n.d	n.d	n.d	n.d	n.d	0.02	n.d	0.01	0.03
PCB 209	0.14	2.38	n.d	n.d	n.d	n.d	n.d	n.d	0.03	0.10	0.09	0.19	0.09	0.02	0.001	0.75	0.27	0.31	0.08	0.12	0.16	n.d	0.01	n.d	0.01	0.04
HCBD	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*		n.d*	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*	
α-HCH	5.99	5.91	2.48	1.73	18.7	18.3	16.5	27.5	0.01	0.03	8.07	n.d	9.6	13.6	0.45	8.81	14.2	14.5	3.90	5.89	3.48	12.8	6.89	3.31	0.02	0.05
Aldrin	n.d	n.d	n.d	n.d	9.24	8.62	10.1	8.66	n.d		1.28	0.02	1.73	7.29	0.51	5.78	3.89	4.49	1.58	0.78	7.21	0.41	1.63	1.68	0.01	0.02
β-HCH	9.9	24.9	11.9	0.01	12.9	12.0	7.30	122	0.00	0.01	n.d*	n.d*	n.d*	n.d*	0.23	10.6	16.2	1.09	2.18	3.66	38.6	178	8.04	1.94	0.01	0.03
cis-chlordane	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d		0.35	n.d	0.55	0.45	0.54	1.69	0.83	0.26	0.74	0.10	n.d	0.08	0.60	0.89	0.01	0.03
Dieldrin	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	17.9	53.7	0.23	n.d	5.65	4.96	2.79	7.24	18.1	15.3	24.7	16.5	79.2	46.0	50.6	46.3	0.003	0.01
Endosulphane	0.60	35.1	0.09	0.11	13.5	13.2	13.0	30.0	0.00	0.01	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	
Endrin	3.78	34.7	1.52	1.47	19.7	16.8	13.8	29.7	0.00	0.01	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	
HCB	16.8	46.3	5.48	44.9	8.40	8.35	19.2	19.0	5.48	16.4	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*	n.d*	15.5	46.5
Heptachlor	n.d	n.d	n.d	n.d	38.4	38.1	54.7	19.1	n.d		0.78	0.11	27.9	2.68	0.72	18.6	0.63	9.38	11.5	2.50	1.41	1.04	1.27	0.15	38.3	115
Heptachlor epoxide	n.d	n.d	n.d	n.d	27.2	27.9	27.9	16.7	n.d		0.36	0.02	0.81	4.19	0.14	0.70	0.02	0.23	0.23	0.19	0.02	0.10	0.07	0.12	0.01	0.04
Lindane	5.25	40.8	8.66	0.36	24.0	23.7	32.2	23.8	0.05	0.16	10.1	0.11	8.73	13.5	0.15	11.5	14.2	10.3	6.59	6.70	6.00	9.5	5.65	1.71	0.01	0.03
op-DDD	10.4	32.2	10.4	3.54	21.1	19.3	8.70	34.4	0.001	0.003	0.04	0.02	0.50	0.13	0.13	8.52	2.52	17.1	1.11	3.27	1.84	2.84	2.38	2.85	0.02	0.06
op-DDE	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d		0.08	0.02	0.32	0.04	0.20	3.13	5.04	5.86	0.07	0.14	0.05	0.31	0.04	0.07	0.01	0.04
op-DDT	11.1	35.3	39.6	39.4	n.d	n.d	n.d	n.d	0.05	0.14	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	
Oxychlordane	5.57	6.56	0.37	35.2	11.7	12.0	9.06	43.5	0.002	0.01	4.50	0.01	1.08	6.34	0.56	1.39	0.35	0.23	1.13	0.45	0.26	1.48	0.72	0.52	48.1	144
pp-DDD	0.56	7.63	5.60	9.02	38.8	39.0	86.0	109	0.01	0.03	0.00	0.02	4.80	0.11	0.65	8.36	30.0	4.63	6.29	6.50	5.78	21.9	11.1	15.8	0.01	0.04
pp-DDE	21.9	25.6	1.81	11.3	16.2	18.2	18.3	13.2	0.01	0.04	0.13	0.02	4.83	0.13	0.27	13.8	17.7	14.4	3.00	14.0	2.58	17.8	12.0	12.6	0.01	0.04
pp-DDT	0.07	4.14	4.98	3.85	62.1	66.9	79.9	87.8	0.01	0.03	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	
Trans chlordane	0.02	0.01	1.33	1.33	36.6	32.1	29.1	35.2	0.07	0.20	0.22	n.d	76.0	0.10	0.13	6.73	0.08	5.40	0.25	0.30	5.91	0.26	0.04	0.17	0.01	0.04
Trans nonachlor	2.90	8.03	3.27	2.86	21.3	28.7	18.5	27.0	0.00	0.01	0.19	0.002	0.40	0.12	0.09	0.32	0.58	0.03	0.49	0.05	0.01	0.22	0.18	0.17	0.02	0.05
BDE 28	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a			0.02	0.39	0.08	0.21	0.40	0.23	0.00	0.22	0.18	0.12	0.34	0.68	0.85	0.29	0.00	0.01
BDE 47	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a			0.15	0.61	0.66	0.13	0.78	2.02	3.83	2.55	1.94	2.22	4.32	2.87	4.97	1.84	0.01	0.03
BDE 100	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a			0.04	0.14	0.17	0.06	0.23	0.59	0.97	0.46	0.21	0.73	0.76	0.63	0.74	0.38	0.04	0.12
BDE 99	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a			0.19	0.35	0.30	0.07	0.13	0.73	1.40	1.60	0.50	1.17	1.62	0.37	1.97	0.39	0.03	0.08
BDE 154	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a			0.11	0.08	0.06	0.05	0.13	0.14	0.09	0.09	0.28	0.23	0.11	0.20	0.22	0.12	0.03	0.10
BDE 153	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a			0.07	0.07	0.07	0.06	0.10	0.12	0.13	0.12	6.38	0.28	0.18	0.85	0.32	0.13	0.05	0.16

n.d – not detected, n.a – not applicable n.d* - interfering peak present in chromatogram

Appendix A.10 Chapter 7 WFD Priority Substances List

Appendix A.10 Table 1 List of WFD Priority substances and substances of Interest including their EQS values and estimated EQS-C_w and applicability for accumulation by passive samplers

No	Compound		CAS no	EQS - inland Waters (ug/L^{-1})	EQS - other Waters (ug/L^{-1})	EQS - C_w (ug/L^{-1})	Applicability For PS
1	Alachlor		15972-60-8	0.3	0.3	0.3	P
2	Anthracene		120-12-7	0.1	0.1	0.09	C
3	Atrazine		1912-24-9	0.6	0.6	0.6	P
4	Benzene		71-43-2	10	8	8	NP
5	BFRs (total)		32534-81-9	0.0005	0.0002	0.0002	C
6	Cadmium			0.08	0.2	NA	NA
7	Chloroalkanes		85535-84-8	0.4	0.4	0.3	P
8	Chlorofenvinphos		470-90-6	0.1	0.1	0.1	P
9	Chloropyrifos		2921-88-2	0.03	0.03	0.03	P
10	1,2-dichloroethane		107-06-2	10	10	10	NP
11	Dichloromethane		75-09-2	20	20	20	NP
12	Di(2-ethylhexyl)phthalate		117-81-7	1.3	1.3	0.8	C
13	Diuron		330-54-1	0.2	0.2	0.2	NP
14	Endosulfan		115-29-7	0.005	0.0005	0.0005	C
15	Fluoranthene		206-44-0	0.1	0.1	0.07	C
16	Hexachlorobenzene		118-74-1	0.1	0.1	0.01	C
17	Hexachlorobutadiene		87-68-3	0.1	0.1	0.1	C
18	Hexachlorocyclohexane		608-73-1	0.02	0.002	0.002	C
19	Isoproturon		34123-59-6	0.3	0.3	0.3	P
20	Lead		7439-92-1	7.2	7.2	NA	NA
21	Mercury		7439-97-6	0.05	0.05	NA	NA
22	Naphthalene		91-20-3	2.4	1.2	1.2	C
23	Nickel		7440-02-0	20	20	NA	NA
24	Nonylphenols		104-40-5	0.3	0.3	0.3	P
25	Octylphenols		140-66-9	0.1	0.01	0.01	P
26	Pentachlorobenzene		608-93-5	0.0007	0.0007	0.0007	C
27	Pentachlorophenol		87-86-5	0.4	0.4	0.4	NP
28	Polyaromatic hydrocarbons						
		Benzo(b)fluoranthene	205-99-2	0.015	0.015	0.005	C
		Benzo(k)fluoranthene	207-08-9	0.015	0.015	0.002	C
		Benzo(ghi)perylene	191-24-2	0.001	0.001	0.00011	C
		Indeno(1,2,3-cd)pyrene	193-39-5	0.001	0.001	0.0002	C
		Benzo(a)pyrene	50-32-8	0.05	0.05	0.017	C
29	Simazine		122-34-9	1	1	1	NP
30	Tributyltin		36643-28-4	0.0002	0.0002	0.0002	P
31	Trichlorobenzenes		12002-48-1	0.4	0.4	0.4	P
32	Trichloromethane		67-66-3	2.5	2.5	2	NP
33	Trifluarlin		1582-9-08	0.03	0.03	0.03	P
1	Carbon-tetrachloride		56-23-5	13	12		NA
2	DDT Total			0.025	0.025	0.025	C
3	Cyclodiene pesticides Total			0.1	0.1	0.1	C
4	Tetrachloroethylene		127-18-4	10	10	10	NP
5	Trichloroethylene		79-01-6	10	10	10	NP

P – possible, C – currently analyses using PSDs, NA – not applicable, NP – not possible

List of Publications

1. P. White, B. Mc Hugh, R. Poole, E. McGovern, J. White, P. Behan, B. Foley and A. Covaci. Application of congener based multi-matrix profiling techniques to identify potential PCDD/F sources in environmental samples from the Burrishoole Catchment in the West of Ireland. Environmental Pollution. 184 (2014) 449 – 456.

2. Covaci, A., Ionas, A., Malarvannan, G., Mc Hugh, B., Poole, R., White, P., Belpaire, C. Identification of unknown Organohalogenated compounds in eel samples from the Burrishoole catchment, Ireland. Organohal. Comp. (2012) 74, 50-54.