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Role of Passive Sampling in Screening and Monitoring of New and Emerging Chemicals

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Roinn Cumarsáide, Gníomhaithe ar son na hAeráide & Comhshaoil
Department of Communications, Climate Action & Environment

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EPA RESEARCH PROGRAMME 2014–2020

Role of Passive Sampling in Screening and Monitoring of New and Emerging Chemicals

(2012-W-MS-11)

EPA Research Report

Prepared for the Environmental Protection Agency

by

Dublin City University

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DISCLAIMER

The EPA Research Programme addresses the need for research in Ireland to inform policymakers and other stakeholders on a range of questions in relation to environmental protection. These reports are intended as contributions to the necessary debate on the protection of the environment.

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Executive Summary

Passive sampling (PS) techniques are rapidly developing as very cost-effective state-of-the-art tools for identifying and measuring ultra-trace micro-pollutants in water. It is possible to obtain improved compound detectability and sensitivity relative to those obtained using more "traditional" spot water sampling and analysis techniques.

On an operational front, a number of questions remain regarding the merits of PS in providing representative sampling of chemicals in environmental waters and the quantification of water column pollutant loadings, and its suitability for adoption for checking legislative compliance.

It is theoretically possible to use PS to quantify and/or screen for the vast majority of organic compounds. However, a number of conditions must be met before PS techniques can be considered fully suitable for the purposes of routine monitoring.

Their application for Water Framework Directive (WFD) (2000/60/EC)[1] purposes requires additional performance criteria. These include the calculation of accurate uptake rates in order to calculate time-weighted average contaminant concentrations in water, and strict protocols for *in situ* deployment.

The primary aim of this project was to gather knowledge (national and international) on the current status of monitoring emerging chemicals in aquatic environments and to assess the value of PS-based techniques for this purpose, particularly within the context of the WFD and the Marine Strategy Framework Directive (MSFD). A further objective was to evaluate the linking of PS-derived concentrations with water and biota environmental quality standards (EQSs). This collaborative project between academic researchers and agencies involved in monitoring water quality involved assessments in 19 different locations in five different counties (Donegal, Mayo, Galway, Cork and Dublin) where water and biota samples were taken and passive samplers were deployed over 3 years. In the Dublin and Cork catchments, studies were carried out over 2 years to assess temporal variations in chemical contamination. Analytical methods for pesticides, pharmaceuticals and non-polar organics were adapted and developed for application to water, biota and passive sampler extracts.

There are still many knowledge gaps and caveats in relation to PS and its use in "compliance monitoring". However, it is evident from this work that, while additional research is required, there is potential for the development of models for assessing the suitability of PS for use in supporting conventional monitoring. There is a need to continue to build PS capacity in Ireland and continued validation of models is required to support operational monitoring. A risk-based approach is recommended, with PS as a tier 1 screening mechanism whereby exceedance of some specific threshold value would lead to further monitoring. There is an ongoing need for inter-laboratory comparison studies to demonstrate competence with PS techniques. Use of polydimethylsiloxane (PDMS) samplers is appropriate for quantitative analysis of a number of non-polar compounds, while polar PS-type devices [e.g. polar organic chemical integrative samplers (POCISs)] can currently be recommended only for the screening of polar compounds. The project team proposes that PS has more obvious applicability in the marine environment; specifically, in trend and offshore monitoring (supporting both the tiered approach and MSFD). In a wider context, as the definition of the biota EQS (EQS_{biota}) embraces other protection goals, i.e. the protection of aquatic life, it is clear that PS can still play a significant role in WFD monitoring.

The project team identified a number of key research gaps, namely in the areas of:

- the development of robust data for accuracy and quality control; robust estimates of partition

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[1] EU Water Framework Directive Monitoring Programme. The EPA is prepared to meet the requirements of the EU Water Framework Directive (2000/60/EC) and National Regulations implementing the Water Framework Directive (S.I. No. 722 of 2003) and National Regulations implementing the Nitrates Directive (S.I. No. 788 of 2005), 2006. Appendix 2.1 – Priority substances and relevant pollutant list for surface waters and groundwater, EPA.

and PS coefficients for performance reference compounds (PRCs);

- ecosystem-specific trophic magnification factor (TMF) and trophic level (TL) data are required to strengthen future assessment outputs, as, presently, there are large uncertainties in this area;
- consistent approaches (and guidelines) for the use of PS in support of monitoring are required.

The project found that PS can be utilised readily for “screening”-based approaches. It is clear that, until PS is seen and validated as a reliable method for monitoring, it will not be used in compliance monitoring. The work in this report relating to cypermethrin shows that there is real potential for investigative monitoring. It is clear from the results that greater dissemination of sampling “success” stories as completed by larger groups and regulators (rather than individual researchers) is needed. We believe that there is a need for European Union (EU)-wide funding in fundamental research on novel receiving phases for polar samplers. Application of polar samplers is generally currently restricted to the investigation of the presence (rather than the quantification) of a wide range of polar compounds, including those that can dissociate. Polar samplers could be used for distribution and fate studies, and screening to determine where further focused monitoring is necessary in environmental management.

This project proposes a “framework tiered” approach, working in tandem with legislative requirements to capitalise on the strengths of PS in assessment processes related to the requirements of the WFD. Ultimately, this project recommends further discussion on a clear national strategy for the applicability of PS techniques (as part of a tiered approach) in water quality monitoring. There is still a significant number of “scientific versus practical” questions remaining to be addressed in order to progress the application of PS methodologies in a “compliance setting”. Ultimately, there is a need for consistency and comparability in the assessment of WFD compliance among the various Member States. A primary focus of this project was to develop the capacity for the use of PS in Ireland by generating pilot information on the applicability of PS in the WFD and by documenting potential roles for PS in Irish waters.

This synthesis report summarises the main aims, methodologies, results and key findings from the project. More details can be found in the end of project report available at http://erc.epa.ie/safer/reports.

1 Background and Objectives

1.1 Introduction

The aquatic environment, including lakes, rivers, ground water, estuaries and coastal zones, is vulnerable to changes induced by human activities. The European Union (EU) Water Framework Directive (WFD) (2000/60/EC) (EU, 2000) aimed to achieve and ensure good ecological and chemical water status and, moreover, to prevent deterioration of freshwater, transitional water and coastal water bodies by 2015. A major difficulty with WFD monitoring is the gathering of representative information on levels of chemical contamination. An associated problem is the development of appropriate analytical methods capable of satisfying the legislative requirements, particularly where acceptable concentrations within the legislation are very low for some compounds. Good chemical status implies compliance with EU environmental quality standards (EQSs) as defined by Annex IX and X of the WFD. Specifically, Annex X of the WFD has identified a list of priority hazardous substances with EQSs for 33 substances set in the WFD Daughter Directive (2008/105/EC). This list has been updated and expanded in a new Daughter Directive (Directive 2013/39/EU) to identify a number of emerging chemicals of concern, including some pesticides and biocides, industrial chemicals and endocrine disruptors. Although Member States can monitor priority substances in “whole” water, biota or sediment, the EQSs are primarily set for the water phase as an annual average (AA) and a maximum allowable concentration (MAC), although biota EQSs (EQS_{biota}) have been established for 11 substances. The new directive also includes the new concept of a “watch list” of substances for which EU-wide monitoring data are to be gathered for the purpose of supporting future prioritisation exercises, and three pharmaceutical substances [diclofenac, 17-β-estradiol (E2) and 17-α-ethinylestradiol (EE2)] are identified for inclusion in the initial list. In March 2015, Commission Implementing Decision 2015/495 was published establishing this watch list with recommended methods of analysis and maximum acceptable method detection limits. Although in the marine environment the WFD requires Member States to achieve chemical status for only territorial waters, the clear link to the WFD pollution methodologies for assessing chemical pollution is enshrined within the Marine Strategy Framework Directive (MSFD) (2008/56/EC), with a specific requirement that contaminant concentrations are measured in a way that ensures comparability with assessments under the WFD (Commission Decision 2010/477/EU).

1.1.1 Monitoring challenges

Many compounds have been shown to have biological effects (e.g. imposex) at trace levels. It can, however, be analytically challenging to achieve sufficiently low detection limits (down to $pg\,L^{-1}$ levels) to measure some priority substances at environmentally and ecotoxicologically relevant concentrations and therefore determine compliance with EQSs. This is especially true for transitional and coastal waters where the EQS requires detection at up to an order of magnitude lower for some substances than for inland waters. Furthermore, infrequent conventional grab sampling does not provide representative information on the chemical quality of a body of water. This strategy is also ineffective in identifying transient pollution events. For example, a study by Williams *et al*. (2003) showed that daily spot samples of waters taken from a river had a wide variance in daily estrone concentrations, ranging from 0.32 to $2.5\,ng\,L^{-1}$. The cost of sampling generally precludes high-frequency sampling and this is particularly the case in coastal waters. This has highlighted the importance of developing methods with lower detection limits and has driven the development of more representative sampling methodologies.

The selection of aquatic biota, such as mussels or fish, as a matrix (as recommended for EQS_{biota}) allows the detection of environmentally relevant concentrations of many lipophilic substances that may not be detectable in the water column and, furthermore, can provide a time-integrated element to sampling insofar as bioaccumulation represents exposure over time. However, there are also practical issues including the difficulties of acquiring suitable target biota samples at some locations and standardising the matrix, for example species selection, size range and age. Moreover, issues such as metabolism and intraspecific biological variability can further confound the comparability of test results.

1.2 Passive Sampling

Passive sampling (PS) is a technique that emerged in the 1980s and is based on the free flow of analyte molecules from a medium being sampled to a receiving medium due to a difference in chemical potentials. PS is proving to be a valuable tool for the monitoring of priority substances in water, sediment and biota and has been identified as a useful complementary technique for use in chemical monitoring. PS methodologies are cost-effective tools for identifying and measuring ultra-trace micro-pollutants in water. They generally allow much greater sensitivity than can be achieved by "traditional" spot sampling, potentially improving detection capabilities by orders of magnitude. PS methods have been applied to a wide variety of compounds, including non-polar organic substances [e.g. polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and polybrominated diphenylethers (PBDEs)], polar compounds (e.g. pharmaceuticals and certain pesticides), trace metals, metalloids, radionuclides and organometallic compounds (e.g. tributyltin), and applications have been widely reported (Vrana *et al.*, 2005). Where EQSs cannot be measured by current analytical methods, PS may provide information to support compliance monitoring. Ongoing developments in areas such as modelling, quality control elements and inter-laboratory comparisons will further validate existing PS techniques, improving their suitability for use in compliance monitoring.

1.2.1 Emerging contaminants

Emerging environmental contaminants are substances that have often long been present in the environment but whose presence and significance are only now being elucidated. Data for emerging substances are often scarce and measurement methods are often at the research and development stage or have not yet been harmonised at EU level. This makes it difficult to interpret and compare the results and represents a major difficulty for regulatory bodies in their decision-making processes. Emerging pollutants can be defined as pollutants that are currently not included in routine monitoring programmes at EU level and which may be candidates for future regulation, depending on research on their (eco)-toxicity, potential health effects and public perception, and on monitoring data regarding their occurrence in the various environmental compartments.

Current legislation on water quality, including the new EU watch list, has introduced a number of new priority substances [including a range of organohalogens, pharmaceutical compounds, endocrine disruptors and brominated flame retardants (BFRs)], as well as the suggested "watch" compounds that are required to be monitored under the WFD. The Network of Reference Laboratories, Research Centres and Related Organisations for Monitoring of Emerging Environmental Substances (NORMAN Network) has also highlighted a comprehensive list of emerging compounds of potential concern (http://www.norman-network.net). The EQS Directive (2008/105/EC) specifies that, in order to monitor compliance of chemical parameters under the WFD, methods of analysis must be able to achieve limits of quantification (LOQs) equal to or below 30% of the associated EQS. For these emerging compounds, extremely low EQS values, especially for marine waters, have been set, which provide a great challenge to the analyst. Loos (2012) has suggested that the extraction of larger volumes of water (10–1000 L) could allow for the achievement of the required LOQs; however, this would be excessively costly and time and labour intensive for most laboratories and would create practical difficulties for sampling.

Owing to the status of "emerging" compounds, in many cases little work on the monitoring of these chemicals in water has been conducted. Of the emerging compounds, PS data are most abundant for the endocrine disruptors; however, many substances have been the subject of few or no reported studies. Much greater research efforts are required on the application of PS for these compounds in water to validate the methods to the level required under legislation. In the report by Loos (2012), the emerging compounds were surveyed for reported analytical methods and it was found that no standard methods existed for the majority of these compounds. In most of the cases, no reported analytical methods had yet been shown to reach the required limits of detection (LODs) for the EQS guidelines. Some work with the PS of emerging compounds has been carried out, with levels of aclonifen, diclofenac, endocrine-disrupting compounds (EDCs) and some organohalogens being determined by polar organic chemical integrative samplers (POCISs) and the levels of some organohalogens determined by semi-permeable membrane devices (SPMDs). The study by Tan *et al*. (2007) investigated endocrine disruptors in wastewater effluent in Australia. They evaluated POCIS results alongside those from grab samples and concluded that, while 1–5 ng L^{-1} method detection limits were achieved for all compounds, the POCIS results demonstrated increased sensitivity compared with those of the grab samples. Mills *et al*. (2011) in a comprehensive review recommended that more work is needed on semi-polar passive samplers. A report by Smedes *et al.* (2010) considers the potential of PS using silicon rubber to meet WFD requirements and lists heptachlor, heptachlor epoxide, bifenox, cybutryn, cypermethrin, dioxins, HBCD, quinoxyfen, dicofol, diclofenac and oestrogens as potentially amenable to this type of sampling. This group continues to research applications of PS to new and emerging compounds.

1.3 Main Objectives

The project described in this report represents an important collaboration between two research centres [Dublin City University (DCU) and the Marine Institute (MI)] together with the Environment Agency for England (EA) and Inland Fisheries Ireland (IFI) to establish the performance and potential of PS as a tool for monitoring emerging contaminants.

This project focused in particular on pollutants listed as Annex X priority substances under the EU WFD. This considered the implications for compliance with current and proposed EQSs and investigated the potential for incorporating PS and biota testing into future compliance, investigative and trend monitoring. The work was underpinned by a number of key studies already carried out by the MI and the EA and an array of literature in the area of priority pollutant monitoring. The impact of this study will be in the implementation of recommendations to improve and facilitate water quality monitoring.

The project aimed to:

- test the use of various PS technologies and biota monitoring in surface water monitoring of priority substances in Ireland;
- establish quantitative and qualitative screening of selected priority substances and proposed priority substances in a number of Irish waters representative of different pressures;
- provide broad qualitative gas chromatography–mass spectrometry (GC–MS) screening for other substances in surface waters;
- assess the status of cypermethrin pollution in selected Irish surface waters;
- carry out a screening study of certain pharmaceutical substances in Irish surface waters;
- develop recommendations and guidelines for the use of PS technologies in future monitoring of surface waters in Ireland.

1.4 Structure of the Report

The synthesis report summarises the main aims, methodologies, results and key findings from the project. This report is divided into five chapters. Chapter 1 provides a background to the project. Chapter 2 describes the methodology used and the results obtained from a number of case studies. Chapter 3 describes the key outputs, followed by conclusions from the work in Chapter 4. The final chapter provides the recommendations from the team on the potential for use of PS in water monitoring. More details can be found in the end of project report.

2 Research Approach: Actions and Results

2.1 Research Approach

2.1.1 The collaboration and work plan

The project was a large-scale collaboration between DCU, MI, EA, IFI and T.E. Laboratories Ltd. Support was also provided at each of the sampling locations by local authorities in many cases. Analytical support was also provided by the Northern Ireland Environment Agency (NIEA). DCU and MI co-ordinated the sampling and deployments over the 3-year project with significant field work carried out in 2013 and 2014. DCU managed the project. Details of sampling site characteristics, analyses developed and conducted, protocols for PS, etc., are given in the end of project report.

This project sought to develop and pilot procedures of sampling and analysis to further enhance the data comparability across participating partners, as well as the integration of PS, water and biota sampling and analysis on a catchment-wide basis. Traditional biota monitoring is often hampered by the diversity of organisms studied and the physiological variability in response to environmental variables, thus complicating comparisons between (eco)-regions, or against suitable assessment criteria or EQSs. Like organisms, PS devices (PSDs) accumulate contaminants over time to similar concentrations and with similar drivers for uptake (Smedes and Booij, 2012). With ongoing research effort and validation, PS therefore has the potential to replace some elements of biota monitoring.

2.1.2 Project elements

This 3-year collaborative research project involved:

- analytical method development;
- PS deployment and analysis of extracts;
- biota monitoring (fish, mussels, eels);
- data integration;
- recommendations on the adoption of PS in a monitoring programme.

2.2 Overview of Passive Sampling

PS is a diffusion-based technique and samplers contain a phase with a high affinity for the target analytes. In some samplers (e.g. low-density polyethylene strips and silicone rubber sheets) this receiving phase is naked, whereas in other samplers (e.g. Chemcatcher and POCISs) it is separated from the bulk water medium by a diffusion-limiting membrane.

Different combinations of membrane and receiving phase allow the sampling device to be tailored to various purposes (Booij and Smedes, 2010). Since the receiving phase is selected to have a high affinity for pollutants of interest, it achieves a higher concentration within the sampler than that in the water phase and can provide significant improvements in analytical detection limits. There are two fundamentally different modes of uptake by receiving phases: absorption [in partition samplers such as polydimethylsiloxane (PDMS) samplers]; and adsorption, when target compounds form strong bonds with the sampling material (e.g. POCISs). A wide range of samplers is available; Seethapathy *et al*. (2008) list 26 different PSDs with reported use in the area of water monitoring alone, each catering to a different range of compounds. The choice of sampler type is generally governed by the hydrophobicity (Log K_{ow}) of the target compounds. Partition samplers have the ability to reach a state of equilibrium depending on the physicochemical properties of the analyte, the structure and properties of the sampler, and the exposure time. The uptake of pollutants by adsorption samplers is more complex and the useful sampling period is limited by the capacity of the receiving phase for a particular analyte. In these samplers, factors such as competitive binding may be important. Kinetic (linear uptake) and equilibrium sampling are the two main regimes in force during PS. Samplers based on the principle of equilibrium sampling are allowed high exposure times or have high uptake rates to achieve equilibrium. Calculation of the concentration of the analyte in the water (C_{water}) is then possible using both its partition coefficient between the water and the sampling device (K_{sw}) and the concentration of the analyte measured in the sampler ($C_{sampler}$) (Booij and Smedes, 2010).

The availability and reliability of partition coefficients for various compounds is of particular importance for the development of PS. A study by Difillippo and Eganhouse (2010) discusses PDMS–water partition coefficients in great detail. The sampling rate (R_s) values for an analyte are calculated based on laboratory calibrations and experiments. However, the use of laboratory-based calibration data is limited because R_s can be affected by temperature and turbulence, which can vary widely under field conditions. For this reason, performance reference compounds (PRCs) are used to provide knowledge of *in situ* sampling rates (Booij and Smedes, 2010).

2.2.1 Advantages and disadvantages of passive sampling

PS techniques show great potential in future monitoring programmes for the screening of priority and emerging compounds in water and could have applications in operational, investigative and surveillance monitoring under the WFD. Time-integrated sampling at low detection limits and *in situ* extraction of analytes mean that the requirements of the WFD may now be met for many compounds (Booij *et al.*, 2006).

PS is also a valuable tool owing to its ability to sample large volumes of water, its ease of deployment and processing compared with water or biota sampling, and its non-mechanical operation, which means that no external power input is required (Harman *et al.*, 2012). PS has the ability to measure the freely dissolved or bioavailable fraction of a compound in water (Vrana *et al.*, 2005; Smedes *et al.*, 2010). This is a measure of the availability of the specific compound to organisms in the environment and applies directly to risk assessment, as the freely dissolved fraction is proportional to the chemical activity of the compound. One important consideration is that passive samplers can provide more representative information than infrequent spot sampling about the concentrations of pollutants in water bodies, particularly where concentrations fluctuate markedly in time.

Under current requirements, however, PS cannot be used for compliance monitoring. A key challenge in using PS as a monitoring technique for emerging contaminants in water lies in meeting the requirements set out under the WFD (2000/60/EC) and the EQS Directive (2008/105/EC). The chemical monitoring remit of the WFD requires monthly samples of surface water to be collected to ensure that the status of each water body can be determined. The currently recognised sampling method is grab sampling, which is both costly and time consuming and may still not be representative of actual conditions. Within this context, it is clear that the deployment of passive samplers to monitor water bodies for longer periods, providing time-weighted averages for priority substances, could be a big step towards the level of monitoring required by the WFD. However, there are still some obstacles to be overcome before PS is considered a viable sampling method for the WFD. Although the risk of toxicity for aquatic organisms is based on the bioavailable or dissolved pollutants in a water body, the EQSs set out in the WFD for priority substances, with the exception of trace metals, are expressed as concentrations in “whole water”. This means that current analysis must include both the dissolved fraction and any suspended matter when used in compliance monitoring. However, for samples in which the levels of suspended solids are low, it is often very difficult to reach the required LODs by conventional means. In this situation, PS could provide a useful alternative, since it will take up the freely dissolved analytes in the water and has been shown to reach generally lower LODs than conventional grab sampling (Vrana *et al*., 2005). Another factor adding to the uncertainty associated with grab sampling is deployment in areas where turbulence in the water may lead to the periodic resuspension of bottom sediments, which would complicate assessments. A study by Stuer-Lauridsen (2005) found that passive samplers have the capacity to monitor over 75% of the organic micro-pollutants listed in the water quality criteria of the EU and the USA and the WFD, and as listed by the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR). This lends support to the consideration of PS as a method of water monitoring under the WFD. A study by Alvarez *et al.* (2005) showed that grab sampling of river water detected only 24 contaminants, while PS (with a POCIS) detected 32 chemicals. However, while non-polar PS (e.g. using silicon rubber) is being investigated as a quantitative monitoring tool for hydrophobic organic contaminants, PS of polar compounds (e.g. using POCISs) requires much more research. Harman *et al.* (2011) recently reported that, even when using PRCs, POCISs are not useful for quantitative analysis of analytes but could find suitable applications as powerful screening tools.

2.2.2 *Quality control in passive sampling*

In order to evaluate the potential of PS as a water quality monitoring tool from a regulatory or enforcement perspective, it is necessary to conduct proficiency tests for quality control. Several inter-comparison studies have been carried out in recent years, including a QUASIMEME proficiency testing scheme for PS carried out between October 2014 and March 2015 for silicone PSDs. In 2010, an inter-comparison study was carried out by AQUAREF to assess the potential role and efficiency of PS for measuring pollutants in surface and coastal waters in the context of the WFD. (NORMAN Network, 2012) The aim of the study was to assess the reliability of the PS method in comparison with the traditional water sampling approach. A number of observations were made from this study including the following: there was an increase in accuracy when the method of introduction of the compound to the PS membrane was improved; the homogeneity of the results was acceptable, although improvements are needed in analytical methodologies; and, for polar compounds, there was higher variability between laboratories while "within laboratory" variability was acceptable. One of the main findings of this study was that, while PS is suitable for measuring many priority substances in water, there are issues with the handling and analysis of samples in complex environmental matrices that hinder the reliability of this type of tool.

2.2.3 *Passive sampling as a surrogate measurement for biota*

EQS_{biota} have been defined for 11 priority substances, or groups of substances, including mercury, hexachlorobenzene (HCB), hexachlorobutadiene (HCBD), PBDEs and PAHs, as well as a number of new priority substances. Article 3 in the EQS Directive (2008/105/EC) states that long-term trend analysis of the concentrations of those priority substances (listed in Part A of Annex I) that tend to accumulate in sediment and/or biota must be completed. The Marine Conventions, such as OSPAR, have established methodologies for biota and sediment monitoring, but the protocols for freshwater monitoring are less well established across Member States. Challenges exist with traditional biota monitoring owing to the diversity of organisms monitored by Member States and the physiological variability in the response to environmental variables. The metabolism, developmental stage and health status of an organism may affect uptake from the environment, and it may be difficult to define *in situ* bioaccumulation factors (BAFs) accurately. Sufficient numbers or size classes of target monitoring organisms may not be available at a particular site in order to conduct an assessment. These factors complicate comparisons between regions or with EAC (Environmental Assessment Criteria)/EQSs. Because of similar drivers for uptake, both organisms and PSDs can accumulate contaminants over time; however, unlike biota, PS has negligible background concentrations and the derived C_{water} is not influenced by physiological or biochemical factors. Therefore, PS allows global comparisons to be made. Strong correlations between mussels and silicon rubber passive samplers for organic compounds, in terms of both concentrations measured and effects, have been reported. Data from 10 years of monitoring in the Netherlands and from a PS trial conducted by the International Council for the Exploration of the Seas (ICES) in 2007 demonstrate a clear relationship between concentrations of PCBs and PAHs in target organisms (primarily mussels) and passive samplers. Mayer and Holmstrup (2008), Smedes *et al.* (2010) and Claessens *et al*. (2015) have all demonstrated potential mechanisms for the conversion of C_{water} into that determined in mussels and, while differences are noted, these are of the order expected from such an exercise. Booij and Smedes (2010) developed a model to compare and contrast the differences in sample matrices using data from studies carried out on hydrophobic compounds in mussels and SPMDs in the Scheldt–North Sea area. The model was capable of describing the concentration ratios of mussels and passive samplers in seven out of nine studies. Issues were experienced because of the variability in mussel BAFs and the water sampling rates of SPMDs. Further research is required in order to develop PS as a surrogate to biota monitoring. Figure 2.1 provides a summary of the project approach to incorporate PS into operational monitoring programmes. Potential exists for PS to be used as an “early warning tool” with PS-specific threshold values, which are lower than the EQSs. When these values are exceeded, full-scale biota monitoring would be required. This has both ethical and economic advantages, reducing the number of organisms sacrificed and the costs because of the simplicity of PS deployment, clean-up and analysis. With ongoing research and further standardisation of protocols, PS has the potential to replace some elements of biota monitoring and act as a support to monitoring objectives for hydrophobic compounds, although additional biota monitoring could still be required to assess the risks of secondary poisoning, including exposure of humans. The tiered approach shown in Figure 2.2 illustrates how PS might be used to determine the ecological relevance of certain chemicals and how PS might reduce the need for biota monitoring in some instances.

2.3 Site Selection

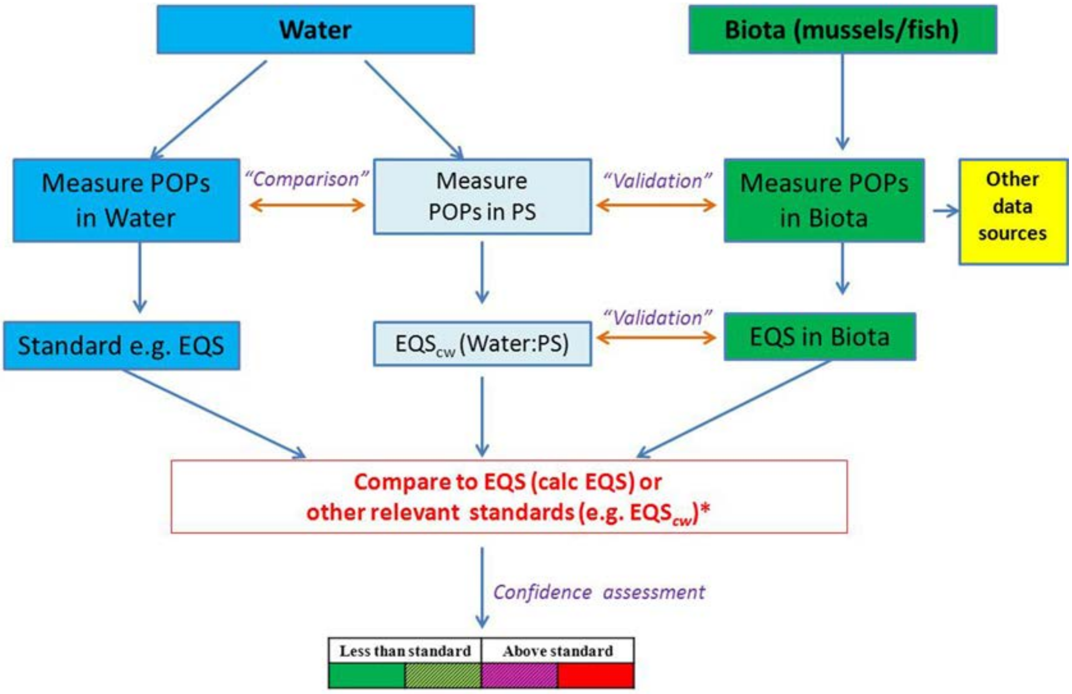
As outlined in the project proposal, a number of specific requirements had to be met by sites to be used in the study. As far as possible, the choice of deployment locations took into account current WFD monitoring to maximise synergies (e.g. with spot sampling data). Practical considerations for site selection for PS deployment included access, security of deployment, options for use of structures for deployment, restrictions on deployment of moorings and tidal range in transitional and coastal waters. The locations of the sites selected and the types of sample collected at each site are outlined in Table 2.1. A map showing the sites is illustrated in Figure 2.3.

2.4 Analyses

2.4.1 Analytical protocol

Water samples

A 1 L grab sample (5 L for pharmaceuticals and EDCs) was collected in shatterproof glass bottles at each sampling point ($n = 3$). These samples were extracted using solid phase extraction (SPE), and analysis was carried out by liquid chromatography–mass spectrometry (LC–MS) or GC–MS depending on the analytes analysed. Full details of analytical methodologies are presented in the end of project report.



* Based on the potential derivation of a passive sampling EQS equivalent EQS(PS).

Figure 2.1. Summary of project approach incorporating PS into operational monitoring programmes.

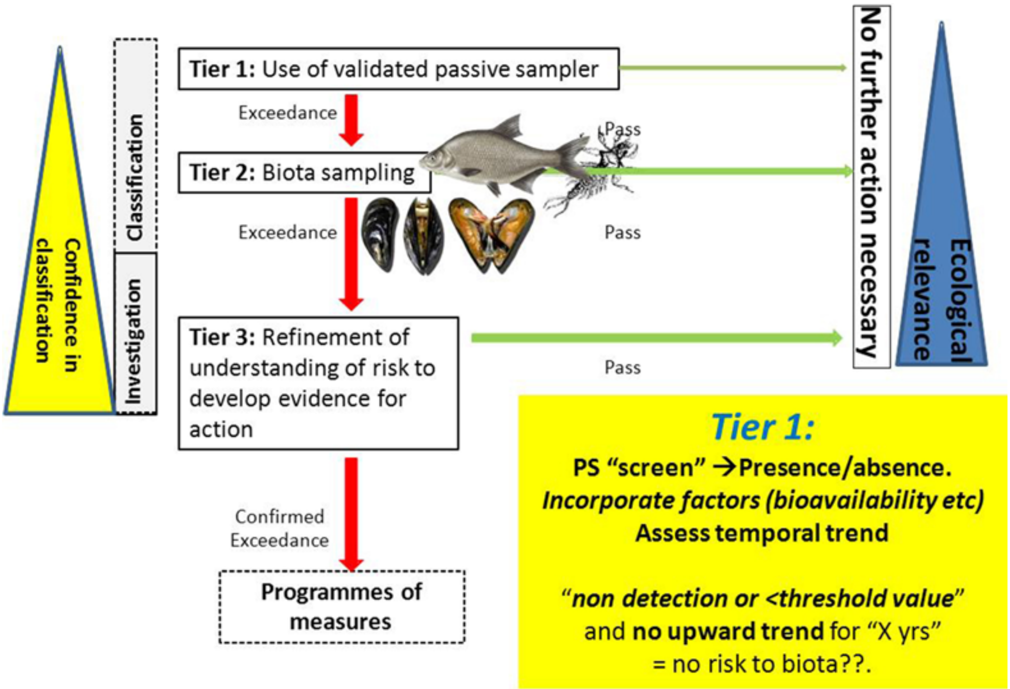


Figure 2.2. Example of a "tiered" approach using PS. Modified from Whitehouse, presented at a workshop "Passive Sampling as a monitoring tool for emerging chemicals", Dublin, personal communication, 2014.

Table 2.1. Overview of sites selected as part of this study and rationale behind selection

County	Site	Rationale	POCIS	PDMS	Water	Mussels	Fish
Cork	Inchigeelagh	Upstream river	✓	✓	✓		✓
	Inniscarra	Downstream river	✓	✓	✓		✓
	Shandon	Riverine/transitional	✓	✓	✓		✓
	Lough Mahon	Riverine/transitional	✓	✓	✓	✓	
	Outer bay	Riverine/transitional	✓	✓	✓	✓	
Dublin	Poolbeg	High-pressure coast	✓	✓	✓	✓	
	Osberstown	Riverine/transitional	✓	✓	✓	✓	
	Lucan Bridge	Downstream river	✓	✓	✓		✓
	Kilcullen Bridge	Upstream river	✓	✓	✓		✓
Galway	Kilkieran Bay	Coastal reference	✓	✓	✓	✓	
Mayo[a]	Burrishoole	Upstream river	✓	✓	✓		✓
Donegal[b]	Glen Lackagh 1	Cypermethrin study	SPMD	✓	✓		
	Glen Lackagh 2	Cypermethrin study	SPMD	✓	✓		

[a] Multiple locations in Burrishoole catchment.

[b] Donegal was added to include three further sampling points; these sites are described in the Cypermethrin case study. Benthic kick sampling was also completed in collaboration with the EPA at these locations.

Passive samples

Extraction from the POCISs and analysis of the extracts was carried out by the EA National Laboratory Service (NLS) in the UK. PDMS samplers were solvent extracted and analysis was carried out by LC–MS or GC–MS depending on the analytes required. Full details of analytical methodologies can be found in the end of project report.

Biota samples

Mussels were collected at coastal sampling sites and three size classes of fish samples were provided by

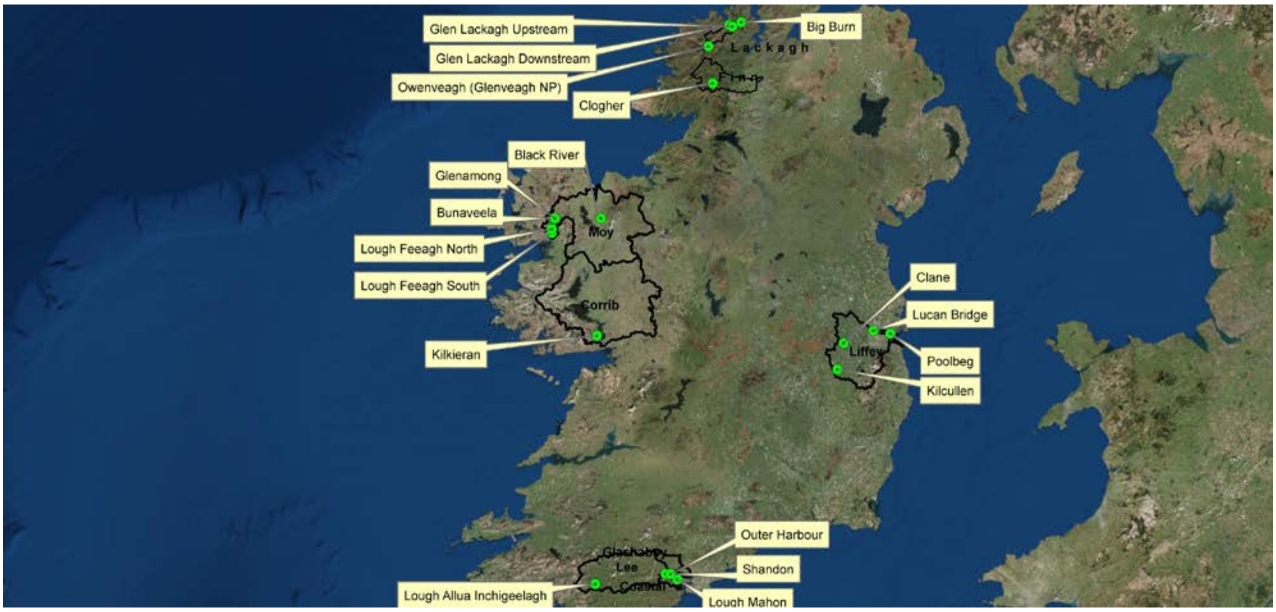


Figure 2.3. Sampling/deployment locations included in this study.

IFI. Summary details of biota sampled (species, etc.) and analysed are provided in Table 2.8.

2.5 Case Study 1: Pharmaceuticals and Endocrine-disrupting Compounds

2.5.1 Background

There is a threat posed to the environment by the occurrence of pharmaceuticals and personal care products (PPCPs). The main source of PPCPs is through the wastewater management systems present in all major urbanised areas. The use of wastewater treatment plants (WWTPs) serves as a means for the removal of organic matter and other substances prior to the discharge of wastewater into the environment, although not all the compounds in the effluent can be removed or degraded to a harmless product. The construction of more WWTPs, under EU regulations, has partly eliminated the discharge of raw sewerage into the environment. The ingestion of pharmaceuticals, and their metabolism (or lack of) and subsequent excretion (generally via urine and faeces), serves as a major route to the environment.

The objective of this study was to screen a number of samples associated with WWTP run-off for pharmaceuticals and steroids, and to assess the value of PS in monitoring these compounds.

2.5.2 Compounds of interest

Three pharmaceuticals have been included on the EU “watch list” (Directives 2013/39/EU and 2015/495/EU) and therefore could, in the future, be added to the priority substances list: hormonal steroids EE2 and E2, and the non-steroidal anti-inflammatory drug diclofenac.

2.5.3 Overall findings and conclusions

This is the first time that pharmaceuticals are being proposed for addition to existing EU water legislation and very low EQS values (often analytically challenging) have been set for many of the proposed priority substances, EDCs and pharmaceuticals. Diclofenac is a non-steroidal anti-inflammatory drug. EE2 is a synthetic estradiol used in contraceptive pills and for the treatment of menopausal and post-menopausal symptoms. E2 is the predominant natural female sex hormone and is the most active of the naturally occurring oestrogenic hormones and is a key intermediate in industrial synthesis of other oestrogens and various hormonal 19-norsteroids.

From the results presented in Table 2.2, it can be seen that pharmaceutical compounds were detected in both water samples and passive samplers collected in 2014 and 2015. As accurate sampling rates for POCISs were not available, levels are presented as ng/device for the PSDs for diclofenac and as estimated

Table 2.2. Concentrations and relative percentage occurrence (brackets) of pharmaceuticals and EDCs along the Liffey catchment in water and passive samples collected in 2014 and 2015

Analyte	Matrix	Kilcullen	Osberstown	Lucan	Poolbeg
2014 results					
Dcl	POCIS	0.66	0.93	17.48	3.32
E1		< 0.23 (65.7)	0.29 (70.7)	0.37 (75.5)	0.42 (82.4)
E2		< 0.06	< 0.06	< 0.06	0.05
EE2		< 0.06	< 0.06	< 0.06	< 0.04
Dcl	Water	4.05	4.17	29.26	3.92
E1		< 0.07 (100)	nd	0.33 (43.4)	1.92 (89.3)
E2		nd	0.33 (100)	0.43 (56.6)	0.23 (10.7)
EE2		nd	nd	nd	nd
2015 results					
Dcl	POCIS	0.93	6.2	5.4	1.7
E1		< 0.23 (65.7)	0.31 (72.1)	0.42 (77.8)	0.41 (75.9)
E2		< 0.06	< 0.06	0.06	0.07
EE2		< 0.06	< 0.06	< 0.06	< 0.06
Dcl	Water	5.25	3.03	26.28	4.1
E1		< 0.23 (65.7)	0.31 (72.1)	0.42 (77.8)	0.41 (75.9)
E2		< 0.06	< 0.06	0.06	0.07
EE2		< 0.06	< 0.06	< 0.06	< 0.06

Concentrations of diclofenac in POCISs are presented as amount (ng/device), while concentrations of E1, E2 and EE2 in POCISs are estimated based on sampling rates. Other results are in ng L^{-1}.

Dcl, diclofenac; E1, estrone; nd, not detected.

concentrations (ng L^{-1}) for the EDCs, with the relative percentage loading of each compound in relation to others being sampled in parenthesis. Concentrations and detection levels as measured in both the PSDs and grab samples are indicative of the potential influence of the presence of large WWTPs along the Dublin catchment. Samples collected at the Lucan sampling point (downstream from the Leixlip WWTP) predominately show the highest levels of compounds of interest in the water phase. This shows that E1 was consistently the compound with the highest loading in the PSDs compared with E2 and EE2. This is consistent when compared with the concentrations detected in water samples, where estrone (E1) was often detected when E2 and EE2 were not. The 5 L grab samples ($n = 3$) collected at each sampling point allowed the achievement of a low LOQ (method LOQ of 0.001 ppm).

From the results of this work, the currently unreliable nature of polar PS was explored, as grab samples often detected oestrogenic events that were missed by the passive samplers. The current study does not demonstrate any advantages of polar PS for pharmaceuticals and EDCs outside screening potential. This is in agreement with findings of a recent position paper arising from a 2014 NORMAN Network workshop (Miege *et al.*, 2015).

2.5.4 Key observations

- EDCs were detected in both water samples and passive samplers in the Dublin catchment.
- PS profiles were representative of those in water samples.
- Diclofenac was detected in samples associated with WWTP outfalls at concentrations below the EQS.

2.6 Case Study 2: Cypermethrin

2.6.1 Background

Cypermethrin is a synthetic, toxicity class II pyrethroid insecticide, which has been produced since the mid-1970s. Although cypermethrin is primarily used in agriculture, it is also used as an insecticide in sheep dipping, as a biocide in wood preservatives and to control sea lice in salmon farming. Cypermethrin is commonly found to enter aquatic ecosystems as a result of soil erosion and run-off from agricultural and forestry applications. Although this synthetic pyrethroid has a low toxicity for mammals and birds, low concentrations of cypermethrin are found to have detrimental effects on aquatic ecosystems, as aquatic invertebrates and fish are highly sensitive to cypermethrin. Cypermethrin has a high lipophilicity, which allows it to bioaccumulate readily in the lipid membranes of fish. As a consequence of its detection at significant concentrations in surface waters throughout Europe, and because of its potential ecotoxicological effects on aquatic ecosystems, cypermethrin is now included in EU legislation as a priority substance (at an extremely low and analytically unachievable threshold concentration, 0.08 ng L^{-1} AA EQS for inland waters).

2.6.2 *Sample collection and analysis*

The sites selected for cypermethrin monitoring were based on Environmental Protection Agency (EPA) invertebrate assessment within the catchment. Initially, sampling for cypermethrin was carried out at one upstream and one downstream site along Glen Lackagh in Donegal in 2014. A second study was carried out in 2015 and included five sampling sites – two reference sites and three "at-risk" sites again in Donegal. Sites were selected based on studies carried out by the EPA. Analysis was carried out by SPE/GC–MS (by the MI and NIEA). Table 2.3 includes results from measurement of samples for a suite of pyrethroids. However, cypermethrin is the focus of this initial survey.

2.6.3 *Overall findings and conclusions*

The sites selected for cypermethrin monitoring were based on EPA invertebrate assessment in the catchment. The results of these assessments indicated a deterioration in water quality, and this prompted the work in this project using PS. The results of this work are presented in Tables 2.3 and 2.4. Cypermethrin was detected in water samples and sampler extracts; however, no reliable correlation was found between the two sets of measurements. More samples are needed to provide a thorough study of the impacts of cypermethrin use.

More elevated analyte levels were detected in May than in July, and the observed levels were lowest in the "low-impact" site; however, pyrethroids were found to be ubiquitous in all samples. From this short study, concentrations were found to be in excess of the AA EQS and MAC EQS (0.6 ng L^{-1}) indicating a risk to waters.

From this initial study, there has been a positive detection of these insecticides in the Glen Lackagh catchment over several sampling occasions. This points to occurrence over a consistently longer time frame and prevalence in the environment resulting from episodic events. Sufficient data are not available to indicate concentrations at this stage, but this is worthy of further study. A control site in the national park in Glenveagh was found to have a positive detection. The pathway for this occurrence is as yet unknown and warrants further investigation.

Table 2.3. Summary of pyrethroids detected in water (ng L^{-1}) and passive samples (estimated concentration, ng L^{-1}) collected in the Donegal catchment over two sampling campaigns (2014)

Analyte	Matrix	Glen Lackagh U/S	Midstream A	Midstream B	Midstream C	Glen Lackagh D/S
Cypermethrin 29/04/14	Water	1.17	NA	NA	NA	1.08
Cypermethrin 22/05/14		1.47	1.67	1.38	1.73	1.78
Cypermethrin	PDMS	++	NA	NA	NA	+++
Cypermethrin	SPMD	<70	NA	NA	NA	<70

D/S, downstream; U/S, upstream; +, degree of positive detection.

Table 2.4. Summary of pyrethroids detected in water (ng L^{-1}) and passive samples (estimated concentration, ng L^{-1}) collected in the Donegal catchment in May 2015 (July 2015 in parenthesis)

Analyte		Glen Lackagh U/S	Glen Lackagh D/S	Clogher Finn	Owenveagh	Big Burn
Transfluthrin	Water	0.32 (0.06)	0.37 (0.11)	0.71 (0.16)	< 0.05 (0.13)	0.20 (0.14)
Bifenthrin		0.04 (0.05)	0.03 (0.05)	0.35 (0.09)	0.04 (0.06)	0.03 (0.08)
λ Cyhalothrin		< 1.25 (< 1.25)	< 1.25 (< 1.25)	< 1.25 (< 1.25)	< 1.25 (< 1.25)	< 1.25 (< 1.25)
Cyphenothrin		< 0.75 (< 0.75)	< 0.75 (< 0.75)	1.93 (< 0.75)	< 0.75 (< 0.75)	< 0.75 (1.10)
Permethrin		< 0.2 (< 0.2)	< 0.2 (< 0.2)	0.7 (< 0.2)	< 0.2 (< 0.2)	< 0.2 (< 0.2)
β-Cyfluthrin		0.28 (< 0.15)	< 0.15 (< 0.15)	< 0.15 (< 0.15)	< 0.15 (< 0.15)	0.82 (< 0.15)
Cypermethrin		2.9 (0.2)	3.4 (1.4)	1.5 (1.2)	0.6 (0.8)	2.0 (< 0.1)
Fenvalerate		5.54 (< 0.35)	9.62 (< 0.35)	8.34 (< 0.35)	6.62 (< 0.35)	13.18 (< 0.35)
Esfenvalerate		< 0.35 (NR)	0.60 (NR)	< 0.35 (NR)	< 0.35 (NR)	< 0.35 (NR)
Cypermethrin	PDMS	< 0.06	nd (< 0.001)	nd (< 0.001)	nd (< 0.001)	nd (< 0.001)

D/S, downstream; nd, not detected; NR, not relevant; U/S, upstream.

2.7 Case Study 3: Polar Emerging Compounds

2.7.1 Background

Pesticides and biocidal products constitute the majority of the emerging compounds (nine) most recently added to EU water legislation (Directive 2013/39/EU). These compounds are the focus of this case study.

This case study focused on:

- plant protection product substances: aclonifen, bifenox, dicofol;
- quinoxyfen;
- substances used in biocidal products: cybutryn, dichlorvos, terbutryn;
- industrial chemicals: perfluorooctane sulfonic acid (PFOS).

These chemicals have a variety of uses, from industrial to agricultural applications. This study involved the collection of passive, grab and biota samples in a catchment and monitoring these compounds for two periods (summer 2014 and summer 2015).

2.7.2 Sample collection and analysis

Passive POCISs were deployed at all sampling locations for a period of 1 month each in summer 2014 and summer 2015. At each sampling event, water samples were also collected and analysed for the compounds of interest. Extraction methods are described in the full final report. Analysis was carried out by GC–MS and LC–MS.

2.7.3 Overall findings and conclusions

The results of this work are presented in Tables 2.5 and 2.6 showing data for 2014 and 2015 for the Dublin catchment and for 2013 and 2014 for the Cork catchment. The targeted pesticides were not detected in many cases and were otherwise present in concentrations below the AA EQS. The analytes were detected using passive samplers in 2014 in the Dublin catchment at Kilcullen, but were absent in 2015. Typically, the analytes were not detected in either water samples or passive samplers in the Cork catchment samples. Based on the results obtained, further studies are recommended for these catchments and also a replacement for the POCISs is suggested.

2.8 Case Study 4: Non-Polar Compounds

2.8.1 Background

The detection of persistent organic substances is a ubiquitous phenomenon in the marine environment. Inputs are from a variety of sources including polluted rivers, direct discharges and atmospheric deposition. Overall, this project reports the measurement of substances of concern in Irish marine and fresh waters, with this case study concentrating on the analysis and assessment of the occurrence of

Table 2.5. Concentrations of pesticides in passive samplers (ng/device) and in water samples (ng mL^{-1}) in the Dublin catchment sites

Analyte	Matrix	AA EQS	Kilcullen	Osberstown	Lucan	Poolbeg
2014 results						
Aclonifen	POCIS (ng/device)		nd	nd	nd	nd
Bifenox			nd	nd	nd	nd
Cybutryn			nd	0.017	nd	nd
Dichlorvos			nd	nd	nd	nd
Dicofol			nd	nd	nd	nd
Heptachlor/heptachlor epoxide			nd	nd	nd	nd
Quinoxyfen			nd	nd	nd	nd
Terbutryn			0.007	0.023	nd	nd
Aclonifen	Water (ng mL^{-1})	120	0.001	0.0009	0.001	nd
Bifenox		12	0.001	nd	0.001	nd
Cybutryn		2.5	0.0004	0.0006	0.0005	0.0003
Dichlorvos		0.6	nd	nd	nd	nd
Dicofol		1.3	nd	nd	nd	nd
Heptachlor/heptachlor epoxide		0.002	nd	nd	nd	nd
Quinoxyfen		150	0.001	0.0007	0.001	0.0003
Terbutryn		65	0.0004	0.0006	0.0006	0.0004
2015 results						
Aclonifen	POCIS (ng/device)		nd	nd	nd	nd
Bifenox			nd	nd	nd	nd
Cybutryn			nd	0.006	nd	0.007
Dichlorvos			nd	nd	nd	nd
Dicofol			nd	nd	nd	nd
Heptachlor/heptachlor epoxide			nd	nd	nd	nd
Quinoxyfen			nd	nd	nd	nd
Terbutryn			0.007	0.031	0.054	0.055
Aclonifen	Water (ng mL^{-1})	120	0.002	nd	nd	nd
Bifenox		12	0.004	nd	nd	0.003
Cybutryn		2.5	0.0007	nd	nd	0.0002
Dichlorvos		0.6	0.0004	0.0005	0.0003	0.0002
Dicofol		1.3	nd	nd	nd	nd
Heptachlor/heptachlor epoxide		0.002	nd	nd	nd	nd
Quinoxyfen		150	0.0065	0.0003	nd	nd
Terbutryn		65	0.0002	nd	0.0009	0.0005

Detection limits for aclonifen, bifenox, cybutryn, dichlorvos, dicofol, heptachlor/heptachlor epoxide, quinoxyfen and terbutryn are 0.5–5.0 ng mL^{-1}.

nd, not detected.

non-polar compounds of concern in biota, water samples and passive samplers. In respect of non-polar compounds, water analysis within this project was restricted to selected spot samples to screen for PAHs and PCBs and to quantify PAH and PCBs using PDMS samplers.

Polychlorinated biphenyls

These are synthetic substances with a molecular structure containing a chlorinated biphenyl ring. PCBs were widely used for a variety of purposes, most notably as dieletrics in electrical equipment such as transformers and capacitors. Restrictions on their use

Table 2.6. Concentrations of pesticides in passive samplers (ng/device) and in water samples (ng mL^{-1}) in the Cork catchment sites

Analyte	Matrix	AA EQS	Inchigeelagh	Iniscarra	Shandon	Outer Harbour	Lough Mahon
2013 results							
Aclonifen	Water	120	nd	nd	nd	nd	nd
Bifenox	(ng mL^{-1})	12	nd	nd	nd	nd	nd
Cybutryn		2.5	nd	nd	nd	nd	nd
Dichlorvos		0.6	nd	0.003	0.0004	0.002	0.003
Dicofol		1.3	nd	nd	nd	0.0002	0.0001
Heptachlor/heptachlor epoxide		0.002	nd	nd	nd	nd	nd
Quinoxyfen		150	1.00	1.50	6.00	0.27	0.87
Terbutryn		65	nd	0.0006	nd	nd	nd
2014 results							
Aclonifen	POCIS		nd	nd	nd	nd	nd
Bifenox	(ng/device)		nd	nd	nd	nd	nd
Cybutryn			nd	nd	nd	nd	nd
Dichlorvos			nd	nd	nd	nd	nd
Dicofol			nd	nd	nd	nd	nd
Heptachlor/heptachlor epoxide			nd	nd	nd	nd	nd
Quinoxyfen			1.00	1.00	0.61	0.93	0.67
Terbutryn			nd	nd	nd	nd	nd
Aclonifen	Water	120	nd	nd	nd	nd	nd
Bifenox	(ng mL^{-1})	12	nd	nd	nd	nd	nd
Cybutryn		2.5	nd	0.0055	nd	nd	nd
Dichlorvos		0.6	0.0013	0.0007	0.0019	0.0005	0.0007
Dicofol		1.3	nd	nd	nd	nd	nd
Heptachlor/heptachlor epoxide		0.002	nd	nd	nd	nd	nd
Quinoxyfen		150	1.00	0.30	5.73	8.00	6.40
Terbutryn		65	0.0001	0.0001	0.0002	0.0001	0.0002

Detection limits for aclonifen, bifenox, cybutryn, dichlorvos, dicofol, heptachlor/heptachlor epoxide, quinoxyfen and terbutryn are 0.5–5.0 ng mL^{-1}.

nd, not detected.

in the USA and Europe were introduced in the 1970s, with use in closed systems such as transformers not permitted since the 1980s in Europe. The EPA has estimated 522,081 litres of PCB-containing holdings in Ireland, which are a potential source for the aquatic environment, for instance if improper waste disposal practices occur. PCBs are persistent pollutants with a tendency to bioaccumulate in fish and shellfish tissues and biomagnify through the aquatic food chain. Certain PCB congeners exhibit a “dioxin-like” toxicity.

Brominated flame retardants

BFRs are used in many products such as textiles and electronic goods. These bromine-containing organic compounds include PBDEs. Different PBDE technical mixtures exist, such as penta-, octa- and deca-bromodiphenylethers (BDEs), and are based on the degree of bromination. The penta- and octa-BDEs are banned in Europe, although the deca–BDE mixture may still be used. Other BFRs include hexabromocyclododecane (HBCD).

Organochlorine pesticides

“Organochlorine pesticide” (OCP) is a broad label for a variety of synthetic substances used for pest control, which are persistent and widespread in the marine environment. Examples include dichlorodiphenyltrichloroethane (DDT), lindane (γ-hexachlorocyclohexane; γHCH) and dieldrin. Their toxicity, persistence and tendency to bioaccumulate have led to a global phasing out of many of these substances and most of the traditional OCPs have been banned in Europe for decades. However, because of their persistence, they can still be detected in the environment, although environmental concentrations are decreasing.

2.8.2 Sample collection and analysis

PDMS passive samplers were deployed at all sampling locations for a period of 1 month each in summer 2014 and summer 2015 (Cork catchment in summer 2013 and summer 2014). For biota monitoring, trout were provided by IFI and, in each case, pooled samples of 10 fish were used (unless otherwise stated).

Eels and mussels were also sampled where available/applicable. At each sampling event, water samples were also collected and analysed for the compounds of interest. Extraction methods are described in the end of project report. Analysis was carried out by GC–MS and LC–MS where appropriate.

2.8.3 Overall findings and conclusions

Results of this work are presented in Tables 2.8 and 2.9. Table 2.8 shows the results from passive samplers and Table 2.9 relates to measurements in biota. PAHs were detectable in all samplers analysed. Total values of the PAH results are provided here; however, the full data set is provided in the end of project report. Similarly, total values are provided for PBDEs and PCBs and these indicate detection in all cases where these analytes were measured.

In all cases, these non-polar organics are detected in biota as expected. Mussels are a reliable biota monitor for marine and brackish waters; however, finding such a reliable biota monitor for the catchment studies is clearly more challenging given the ecosystem-specific sampling variabilities introduced [e.g. mobility of organisms, size, species, sex and trophic level (TL)].

Figure 2.1 illustrates how PS in the case of this group of pollutants has real potential to inform risk-based studies. Figure 2.2 shows that a tiered approach can be used and this proposed approach is dealt with in more detail with examples in Chapter 5.

Table 2.7. Details of compounds in Tables 2.8 and 2.9

Abbreviation	Compounds
CCDAN	Cischlordane
DDEPP	p,p’-DDE
DDTPP	p,p’-DDT
HCEPC	α-cis-heptachlorepoxide
HCHA	α-hexachlorocyclohexane
HCHB	β-hexachlorocyclohexane
HCHG	Lindane
HEPC	Heptachlor
OCDAN	Oxychlordane
TCDAN	Transchlordane
TDEPP	p,p’-DDD
TNONC	Transnonachlor

Table 2.8. Dissolved concentration for organic compounds (pg L^{-1}) in PDMS samplers at selected locations

Site	Year	Sum 7 PCBs	Sum 14 PAHs	Sum 6 PBDEs	HCBD	HCB	HCHG	HEPC	OCDAN	HCEPC	TNONC	TCDAN	CCDAN	DDEPP	TDEPP	Cypermethrin
Kilkieran	2013	<11.4	<9080	<5.39	NA	<1.0	<40	<1.0	<0.20	NA	<0.12	<0.20	<1.0	<1.0	<1.0	
Shandon boat club	2013	43.2	10701	NA	<5.70	<1.0	<2027	<1.0	<1.0	0.04	0.02	0.13	<1.0	NA	6.18	
Lough Allua, Inchigeelagh	2013	20.7	171	NA	<0.60	<1.0	<146	0.21	<1.0	<1.0	0.12	<1.0	<1.0	0.64	2.48	
Shandon boat club	2014	<0.37	668	NA	<1.35	<1.0	NA	NA	<1.0	<1.0	<1.0	<1.0	0.08	<1.0	<1.0	
Lough Mahon (bottom mooring)	2014	<1.95	880	NA	0.38	<1.0	<2509	NA	<4.40	0.12	<1.0	<1.67	0.14	17.8	1.08	
Lough Mahon (top mooring)	2014	<1.84	1345	NA	<0.52	<1.40	<2510	NA	<1.0	<4.75	<0.04	<1.0	0.29	NA	1.27	
Inchigeelagh	2014	<1.35	288	NA	<0.79	<1.0	<1.0	NA	8.72	<1.0	<1.0	0.31	<1.0	2.93	<1.0	
Cork (outer harbour)	2014	<1.42	415	NA	<1.0	<1.0	<371	NA	34.8	<1.0	<1.0	0.2	<1.0	<1.0	0.64	
Upstream reference	2014	15.1	1841	NA	<1.0	<1.0	<1.0	0.05	1.22	<1.0	0.4	0.28	0.62	0.57	0.51	
Glen Lackagh Bridge	2014	<16.5	1147	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
Lough Feeagh north	2014	<3.68	100	NA	<1.0	<1.11	NA	0.25	NA	0.38	0.07	0.09	<0.19	0.81	0.2	
Lough Bunaveela	2014	<5.87	291	NA	<3.04	<0.35	NA	<1.0	NA	1.26	<1.0	0.49	0.68	0.02	<1.0	
Lough Feeagh south	2014	<3.07	176	NA	<0.66	<1.0	NA	<1.0	0.02	<1.0	0.18	<1.0	1.1	<1.0	<1.0	
Black River	2014	<3.35	181	NA	<1.0	<1.14	NA	0.71	<1.0	NA	0.18	0.9	<1.0	0.22	NA	
Kilkieran	2014	4.95	247	NA	<1.0	<0.15	<24.4	<1.0	0.47	<1.0	0.08	<1.0	0.06	NA	<1.0	
Kilcullen Bridge	2014	<2.83	1500	NA	<1.0	<1.0	<1.0	<1.0	5.01	<8.19	<0.007	0.19	<1.0	0.23	0.19	
Lucan Bridge	2014	<9.39	2465	NA	<1.0	<0.06	<3381	<1.0	1.83	3.27	0.49	<1.0	<1.0	1.9	<1.0	
Poolbeg	2014	28.3	4806	NA	<1.0	<10	<36	<2.30	0.6	<1.0	<1.0	<1.0	<1.0	0.86	<1.00	
Poolbeg	2015	<2.14	3880	<0.62	<1.0	<7.77	<1288	<1.0	<1.0	1.61	0.11	1.23	0.08	1.78	<13.4	<0.003

Table 2.8. Continued

Site	Year	Sum 7 PCBs	Sum 14 PAHs	Sum 6 PBDEs	HCBD	HCB	HCHG	HEPC	OCDAN	HCEPC	TNONC	TCDAN	CCDAN	DDEPP	TDEPP	Cypermethrin
Lucan Bridge	2015	< 2.04	9183	< 0.23	< 1.0	< 0.27	< 587	0.2	1.33	0.51	0.01	< 1.0	< 1.0	0.61	<9.9	nd (< 0.001)
Clane	2015	< 2.09	7180	< 0.43	< 1.0	< 2.32	< 242	NA	1.04	0.01	0.35	< 1.0	0.14	0.25	< 14.8	nd (< 0.001)
Kilcullen	2015	1.89	6222	< 0.72	<61.0	< 0.77	3.78	< 1.0	1.97	< 1.0	0.01	0.14	< 1.0	< 1.0	<4.32	nd (<0.001)
Clogher (Finn)	2015	< 2.27	900	< 0.33	< 1.01	< 0.66	< 1.0	0.04	0.21	0.83	0.06	0.26	< 1.0	< 1.0	< 10	nd (< 0.001)
Owenveagh (Glenveagh NP)	2015	< 1.49	151	< 0.62	0.33	<4.26	57.6	NA	3.5	0.58	0.09	0.04	<1.0	<0.13	<1.0	nd (<0.001)
Big Burn	2015	< 2.93	1985	< 0.63	< 1.0	< 0.84	1.7	0.12	< 1.0	< 1.0	< 0.25	0.1	< 1.0	< 1.0	0.56	nd (< 0.001)
Glen Lackagh Downstream	2015	< 2.09	2325	< 0.25	< 1.0	< 0.63	7.33	0.66	0.41	0.72	0.04	1.03	< 1.0	< 1.0	< 10.0	nd (< 0.001)
Glen Lackagh Upstream	2015	< 1.04	1631	< 0.16	< 1.0	< 1.86	8.89	NA	0.32	0.01	0.01	0.09	< 1.0	0.9	< 17.6	< 0.06

Details of compounds are given in Table 2.7. Sum 7 PCBs: sum of 28, 52, 101, 118, 153, 138 and 180; sum 14 PAHs: sum of US-EPA 15 PAHs excluding naphthalene; sum 6 PBDEs: sum of 28, 47, 99, 100, 153 and 154.

NA, not analysed; nd, not detected.

Table 2.9. Concentrations of selected organic contaminants in biota (ng g^{-1} wet weight) collected during this project

Site	Year	Matrix	Sum 7 PCBs	Sum 6 PBDEs	HCBD	HCB	HCHG	HCHA	HCHB	HEPC	HCEPC	TNONC	TCDAN	CCDAN	DDEPP	TDEPP	DDTPP	Dichlorvos	PCB	Endosulphan
Bunaveela	2014	Eel	3.76	1.28	0.04	<0.30	<0.30	<0.20	<0.19	<0.12	NA	NA	NA	<0.56	2.60	1.21	0.91	<0.01	<0.11	<0.48
Lough Feeagh	2014	Eel	3.33	0.59	<0.11	<0.78	<0.30	<0.20	NA	<0.14	0.03	<0.07	0.03	<0.37	1.61	0.21	0.39	<0.02	<0.02	<0.35
Glenamong	2014	Eel	1.54	1.63	0.01	<0.31	<0.30	<0.20	<0.19	<0.05	NA	0.04	0.03	<0.18	0.49	0.07	0.13	<0.01	<0.01	<1.11
Mill Race lower	2014	Eel	15.5	0.76	0.004	<0.30	<0.30	0.06	<0.16	<0.01	0.03	NA	0.18	<0.32	2.70	0.03	0.64	<0.01	<0.01	<0.25
Mill Race upper	2014	Eel	7.28	1.12	0.009	<0.30	<0.30	<0.10	<0.13	<0.02	0.04	NA	0.17	<0.07	1.14	1.04	0.86	<0.07	<0.01	<0.10
Shramore Eel	2014	Eel	1.70	0.59	0.10	<0.21	<0.30	<0.21	<0.22	NA	NA	NA	<0.09	<1.05	1.78	0.87	0.23	<0.06	<0.17	<1.58
Goulaun	2014	Eel	2.45	0.89	0.11	0.34	<0.30	0.04	0.04	<0.13	0.04	NA	0.06	<0.61	1.74	0.76	1.56	<0.05	<0.18	<0.28
Feeagh[a]	2014	Trout	0.92	0.26	0.07	<0.39	<0.10	<0.20	0.11	0.05	0.02	0.09	0.007	0.01	0.21	0.35	0.96	<0.03	<0.02	<0.08
Glenamong[a]	2014	Trout	1.44	0.41	0.08	<0.73	0.07	NA	<0.13	<0.07	<0.07	0.08	0.01	0.02	0.11	0.21	0.03	<0.23	NA	<0.12
Shramore/ Goulaun*	2014	Trout	1.12	0.61	0.03	<0.45	<0.10	<0.20	0.08	0.04	0.03	0.12	0.01	0.03	NA	0.07	0.05	<0.04	<0.05	<0.14
Bunaveela[a]	2014	Trout	0.92	0.50	0.03	<0.67	<0.10	<0.20	NA	0.02	0.04	0.02	0.01	0.03	0.65	0.49	0.01	<0.06	<0.03	NA
Lough Mahon[a]	2014	Mussels	13.3	3.03	0.003	0.05	0.09	<0.15	<0.02	<0.13	0.005	0.13	0.05	0.13	<3.10	0.03	0.02	<0.01	<0.01	NA
Poolbeg[a]	2014	Mussels	4.66	2.52	0.04	0.12	<0.30	<0.15	0.05	<0.22	<0.10	0.07	0.03	0.06	<1.22	0.86	0.05	<0.04	<0.01	<0.04
Carragh pooled	2015	Trout	1.94	5.34	0.01	0.30	<0.20	<0.20	<0.29	<0.11	0.03	0.05	0.01	0.01	<2.11	NA	<0.17	<0.02	<0.04	<0.49
Clane Bridge[a]	2015	Trout	1.36	4.58	0.008	0.29	0.138	<0.20	NA	<0.10	0.02	0.05	0.008	0.01	<3.13	NA	<0.14	<0.01	<0.05	<0.23
Celbridge Weir[a]	2015	Trout	2.77	7.83	0.13	0.31	<0.43	<0.20	<0.19	<0.08	0.05	0.09	0.015	0.02	<5.36	NA	<0.33	<0.04	<0.11	<0.35
Newbridge[a]	2015	Trout	1.70	3.13	0.03	0.31	<0.35	<0.20	<0.09	<0.12	0.04	0.06	0.03	0.01	<3.65	NA	<0.40	<0.04	<0.03	<0.12
Chapelizod[a]	2015	Trout	6.21	8.89	0.09	1.10	<0.10	<0.20	0.09	<0.35	0.01	0.09	0.01	0.02	<3.9	NA	0.27	<0.02	<0.18	<0.29
Chapelizod (*n* = 1)	2015	Trout	5.74	7.13	0.02	0.99	<0.10	NA	<0.20	<0.08	0.03	0.1	0.03	0.03	<3.22	NA	<0.37	<0.03	<0.21	<0.15
Chapelizod (*n* = 1)	2015	Trout	7.78	8.42	0.05	1.05	0.06	<0.20	0.11	<0.19	0.09	0.09	0.04	0.04	<3.80	NA	0.27	<0.04	<0.18	<0.36
Chapelizod (*n* = 1)	2015	Trout	6.54	6.98	0.02	0.39	0.15	<0.20	0.04	<0.19	0.03	0.08	0.01	0.01	<2.96	NA	0.35	<0.10	<0.07	<0.11
Chapelizod (*n* = 1)	2015	Trout	6.48	8.04	0.02	0.99	<0.10	<0.20	0.15	<0.23	0.04	0.09	0.04	0.01	<3.13	NA	0.29	<0.08	<0.19	<0.23
Chapelizod (*n* = 1)	2015	Trout	6.56	8.07	0.03	0.77	<0.10	<0.20	<0.12	<0.25	0.06	0.09	0.03	0.02	<3.29	NA	0.63	<0.11	<0.19	<0.25

Details of compounds are given in Table 2.7. Sum 7 PCBs: sum of 28, 52, 101, 118, 153, 138 and 180; sum 6 PBDEs: sum of 28, 47, 99, 100, 153 and 154.

[a] Pooled sample (*n* ≥ 10 fish or *n* = 50 mussels).

NA, not analysed.

3 Key Project Outputs

The outputs of this project include the generation of new information on the use of PS for emerging contaminants with (where applicable) concurrent analysis of water and biota in freshwater and marine environments.

Analytical methods for the determination of emerging contaminants, including pesticides, EDCs, PAHs and PFOS, were adapted from methods described in the literature and the project team are publishing improvements in current methods (see end of project report for references). During the project, two workshops were held and stakeholders and other researchers were invited to discuss the topic of PS in monitoring. The aims of these workshops [attended by representatives from the EPA, the NIEA, DCU, the then Department of the Environment, Community and Local Government,[2] the University of Portsmouth/SWIFT-WFD[3] and the Research Centre for Toxic Compounds in the Environment (Recetox)] were to discuss the merits of PS and the potential of a tiered approach.

The aims were achieved by:

- outlining the scope of the EPA-funded project entitled 'The role of passive sampling in the screening and monitoring of new and emerging chemicals' by the project team;
- gathering knowledge (national and international) on the current status of information on emerging chemicals and PS;
- discussing the use of PS in operational monitoring of legacy, and new and emerging chemicals, particularly in respect of the WFD and the MSFD;
- discussing the merits of treating passive samplers as a screening matrix as part of a tiered approach to compliance monitoring.

This project has provided postdoctoral research training opportunities, including project management training, generic research skills training and analytical skills training, to four researchers in the project team, building the capacity for both analytical science and environmental monitoring in Ireland. The project has become an important sounding board for parallel emerging contaminants projects in the EPA and local authorities. Important relationships have been established between key stakeholders in Ireland, providing the potential for future collaboration on environmental research. This, together with international engagements during this and other projects, has provided the opportunity for national and EU research funding in the future. The following project resources and outputs are also available:

- published papers (available at http://erc.epa.ie);
- raw analytical data sets (available at http://erc.epa.ie);
- the project website (https://sites.google.com/site/irishpassivesampling/).

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[2] Now known as the Department of Housing, Planning and Local Government.

[3] SWIFT-WFD: Screening methods for Water data InFormaTion in support of the implementation of the Water Framework Directive.

4 Conclusions from Research and Future Research Needs

The end of project report provides detailed methodologies, site information (e.g. catchment practices, traffic and rainfall data) and analytical concentration data (pesticides, PCBs, PAHs, PBDEs) measured in a wide range of environmentally relevant matrices (water, biota and PSDs). This synthesis report provides a very valuable resource that informs agencies, local authorities and other researchers of further research needs and details the potential future direction of monitoring practices in Ireland.

At the conclusion of the project, it is proposed that:

- There is a role for PS in both screening and trend monitoring in feeding into “tiered” risk-based approaches to WFD monitoring. It is clear, however, that, until PS can be demonstrated to be a validated and reliable method for monitoring, it is unlikely to be used in compliance monitoring.
- While water, sediment and biota are the matrices of relevance for the WFD, with appropriate validation, for selected compounds, PS shows potential to provide pollutant burden information that is at least as representative as that from “conventional matrices”.
- Working in tandem with EU guidance documentation, there is a need to close up biota/PS validation gaps, work on statistical aspects of WFD monitoring and develop shared monitoring tools for use at EU level.
- The potential for the inclusion of PS as a stand-alone matrix for WFD monitoring is high (particularly in marine environments where representative samples can be difficult to obtain, sampling costs are high and EQSs are often a factor of 10 lower than for freshwater). The concurrent development of supporting EQS_{cw} or threshold values for some compounds may provide solutions to current (and future) ultra-trace EQS-related analytical difficulties.
- The potential for information generated from PS to support WFD (and MSFD) monitoring is now such that there is an ongoing need to further enhance both national and international capacity-building elements in the area of PS research and development.
- There is a clear need to continue to build PS capacity in Ireland and for the ongoing validation of the models to support operational monitoring.
- Further to this, it is only through focused, integrated multi-state research and monitoring initiatives that it will be possible to provide greater validation linking PS and biota, potentially ultimately leading to the development of widely accepted stand-alone EQS_{cw} (concentration in water) suitable for supporting compliance goals.

5 Recommendations for Implementation and Uptake of Research Findings

5.1 Background

This work shows the need for the improved standardisation of approaches and methodologies, and improved analysis and quality control with regard to PS. From the investigations of work to date, it is clear that PS can play an important role in the screening of waters for emerging contaminants. This is especially the case for hydrophobic substances, where they could be incorporated into a risk-based approach to monitoring (Figure 2.2). Further, it has been demonstrated that PS has a role to play in trend monitoring to determine where waters are improving (or deteriorating) in quality over time, thereby offering the WFD monitoring programme a valuable tool.

PS for the risk assessment of contaminated sediments has proved to be a successful means of assessing sediment toxicity and bioaccumulation. In recent years, significant developments in PS models for the water column have improved *in situ* calibration. Gaps still remain, however, in respect of the generation of robust data to increase accuracy, to provide quality control and reliable estimates of partition coefficients, and to facilitate the use of PRCs.

According to the European Commission technical guidance for the implementation of EQS_{biota}, PS can be applied in a tiered approach to identify or rank areas of potential EQS exceedance (Figure 2.2). In such a tiered approach, trigger values (i.e. threshold concentrations, the exceedance of which triggers the second tier monitoring of biota) are needed and research to develop these would be worthwhile. If EQS_{biota} values were set only to protect human health from exposure via the consumption of fish, there would be no role for PS in water monitoring. In this case, it would be sufficient to assess whether or not levels of contaminants in fish used for human consumption exceed the defined thresholds. However, since the definition of EQS_{biota} also embraces other protection goals, including the protection of aquatic life, PS can still play a significant role in WFD monitoring. According to the WFD, it is allowable to convert EQS_{biota} values to equally protective water EQS (EQS_{water}) values and use such standards in regulatory monitoring. The uncertainty of PS concentrations of the most hydrophobic priority substances in water is sufficiently low to allow, in principle, for a comparison with EQS_{water}. This is possible especially because LOQs that are achievable by PS for those hydrophobic compounds are lower than the corresponding EQSs. Ongoing research is required to continue to develop this potential. This project has supported other study findings in demonstrating good relationships between C_{free} (free concentration) and lipid-normalised concentrations in mussels, suggesting that PS can be used to predict C_{biota} (concentration in biota) at lower TLs.

The picture is less clear on whether or not similar relationships/models are achievable for other higher TLs. In order to enhance its promising features further, a greater level of research is needed to assess how PS measurements can best be linked to concentrations at higher levels of the aquatic food web. Combining PS data and bioaccumulation models provides a theoretical basis for assessing and predicting bioaccumulation in biota; however, the introduction of biological and spatial variables into models adds high levels of uncertainty. Trophic magnification is ecosystem specific and can vary greatly between locations. The use of generic literature values for the trophic magnification factor (TMF) and the TL often does not improve the results of assessment. Ecosystem-specific TMF and TL data are required to strengthen future assessment outputs, as presently there are great uncertainties in this area. However, these issues also present inherent challenges in biota monitoring, as suitable target species representing TL4, as required by the WFD, may not be available.

5.2 Application of Passive Sampling in a Tiered Approach to Monitoring: A Model Way Forward?

The extrapolation of “free dissolved” PS information beyond its pure scientific merits is proving to be a significant barrier to PS (of hydrophobic pollutants) becoming recognised as something other than a complementary technique to spot sampling. Spot sample collection and analysis to support the requirements of the WFD often pose significant challenges in an analytical context because of the frequency of sampling, the low concentrations (ppt) of the analytes, the amount of matrix required and the complexity of the matrices used.

It is well documented that samples represent the environment at a specific time and place. Monteyne *et al.* (2013) note that the marine ecosystem is a complex and dynamic system influenced by tides, currents, river discharges and point sources, such as harbours, marinas and boat traffic routes. Therefore, analytical measurements of organic micro-pollutants in marine ecosystems are often not easy to interpret in the context of trend monitoring and environmental risk assessment. The authors note that one possible way to overcome these issues is through the considered use of passive samplers.

Marine EQS thresholds are often an order of magnitude lower than freshwater values to account for trophic magnification from top predators. This background and information available in the literature provided the basis for the focus of this project on the possible application of PS to support marine assessments. The relationship between freely dissolved concentrations, derived from PS data, and mussel concentrations in the project coastal reference location at Kilkieran is demonstrated for a variety of hydrophobic pollutants in Figure 5.1.

A recent publication by Brack *et al.* (2017) notes that practical implementation of the WFD with regard to chemical pollution has faced some challenges. The authors (in support of the upcoming WFD review in 2019), in discussing a research project entitled “SOLUTIONS”, and the European monitoring network NORMAN, have evaluated the state of the art of the science in respect of the WFD. Ten recommendations to improve monitoring and strengthen comprehensive prioritisation, foster consistent assessment and support solution-oriented management of surface waters are discussed.

The integration of effect-based tools, the application of PS for bioaccumulative chemicals and an integrated strategy for the prioritisation of contaminants, accounting for knowledge gaps, are seen as important approaches to advance monitoring. Including all

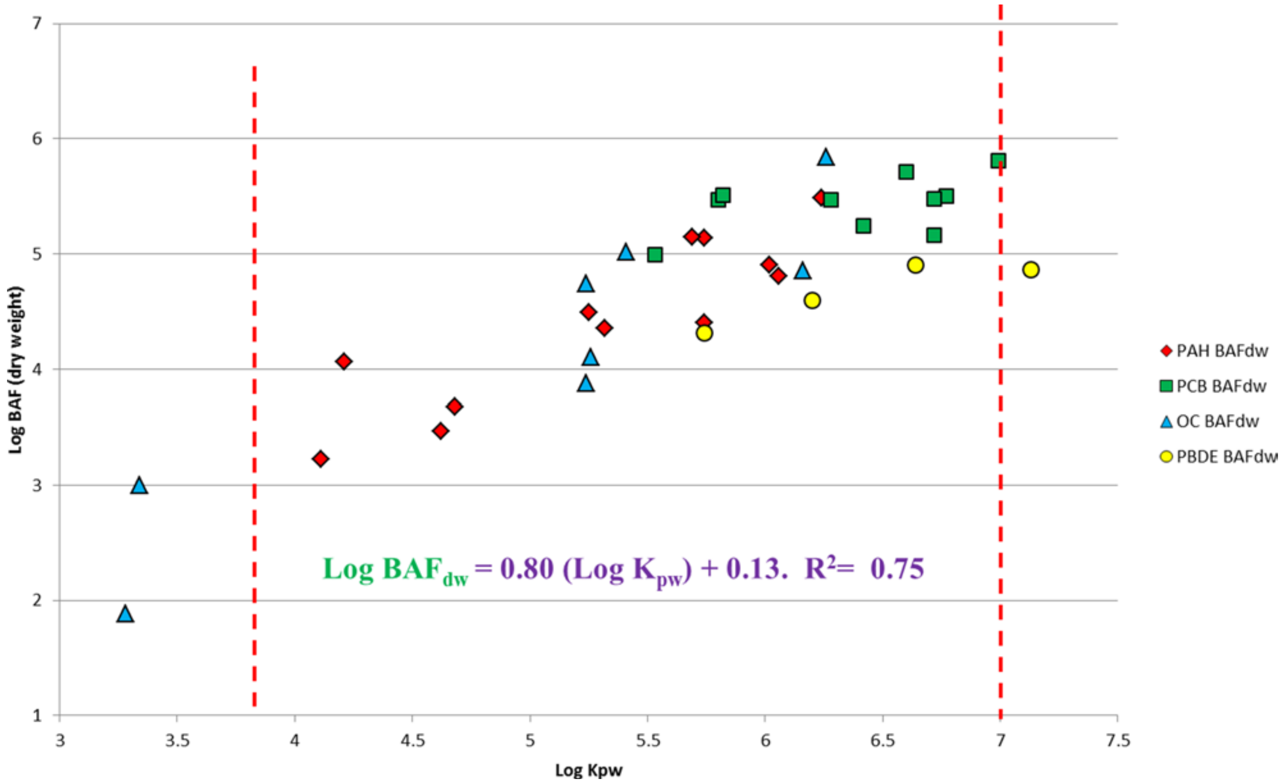

Figure 5.1. Relationship between mussels (log BAF dry weight) and PDMS-dissolved concentrations at coastal reference site in Kilkieran.

relevant chemical contaminants in more holistic "chemical status" assessments, using effect-based trigger values to address priority mixtures of chemicals to better consider historical burdens accumulated in sediments and using models to fill data gaps are recommended for a consistent assessment of contamination. It is clear from this report that PS (and passive dosing) has a significant role to play in solution-oriented management and as part of a tiered approach in investigative monitoring to identify toxicity drivers, strengthen consistent legislative frameworks and apply solution-oriented approaches that explore risk reduction scenarios before and along with risk assessment.

5.3 Rationale and Methodology: EQS$_{biota}$ and a Role for Passive Sampling

The derivation of EQS thresholds considers direct ecotoxicity to aquatic organisms, exposure to humans through consumption of fish and fishery products, and exposure to predators through secondary poisoning. The most critical of these routes determines the final standard. For compounds that have a strong potential to bioaccumulate in fish, human fish consumption and secondary poisoning routes are often most critical. Because of the characteristics of these compounds, concentrations increase along the food chain.

Concentrations in TL4 fish (as shown in Figure 5.2) depend on the accumulation of substances from the aqueous phase by lower aquatic organisms [bioconcentration factors (BCFs)] and accumulation in the food chain from TL1–3 to TL4 [biomagnification factors (BMFs)].

The combination of BCF and BMF processes is represented by the BAF (see Figure 5.2). Further details of this approach are included in the full report.

In order to establish an equivalently protective EQS for all biota, taxon adjustment of monitoring data to account for trophic magnification is required. To ensure consistency in approaches between individual countries, the EU has recently described a procedure (via Technical Guidance Document No 32)[4] for data preparation prior to compliance assessment. This stepwise process of adjusting monitoring data to an appropriate TL (TL4) requires that monitoring data (concentrations in muscle or whole organism on a wet-weight basis) be adjusted to account for a number of factors. Therefore, a single value is derived and expressed in the context of fish of TL4. This process of adding additional "biological" and "spatial" variables to assessments adds additional levels of uncertainty to assessment processes.

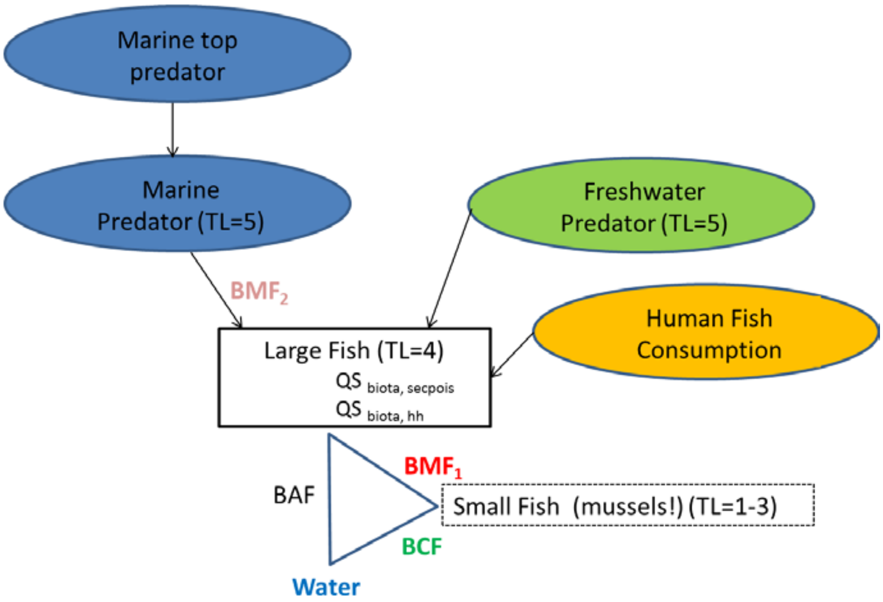

Figure 5.2. Accumulation in the aquatic environment. Adapted from Moermond and Verbruggen, 2013. QS$_{hh}$, quality standard for human health; QS$_{secpois}$, quality standard for secondary poisoning.

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[4] https://echa.europa.eu/documents/10162/16960216/tgdpart2_2ed_en.pdf

5.4 Normalisation of Monitoring Data for EQS_{biota} Assessment

The stepwise process of adjusting biota monitoring data to an appropriate TL (TL4) prior to assessment relative to the EQS_{biota} requires that monitoring data in muscle or whole organisms such as mussels (on a wet-weight basis) be adjusted to account for a number of factors and, according to the abovementioned technical guidance document, this should be completed as follows:

$Conc_{TL\text{-}adj} = Conc_{meas} \times TMF^{(4-TL(x))} \times$ default dry weight/actual dry weight

Where:

$Conc_{TL\text{-}adj.}$ = concentration after normalisation to dry weight (0.26 for fish or 0.083 for mussels);

$Conc_{meas}$ = concentration of HCB in individual samples;

TMF: e.g. HCB ≈ 3.0 (range 1–6) (Moermond and Verbruggen, 2013);

TL(x) = species TL for mussels = 2.1 (fishbase).

5.5 Methodology: Passive Sampling to Assessment Support?

Smedes and Booij (2012) describe the general process by which PDMS passive samplers were used to estimate freely dissolved hydrophobic contaminant concentrations (see Table 2.6) in the water column at a variety of Irish locations. As part of this process, site-specific PRC sampling rate curves were generated (see example for Poolbeg in Figure 5.3) for a variety of organic pollutants at each test site.

Using PS data and building on literature (TMFs and mussel/PS relationships) there is potential for the development of a "pilot" model/toolkit to "back-extrapolate" EQS_{biota} to equivalent PS "threshold" values. As noted by Booij *et al.* (2006), extrapolation of PS biota relationships beyond lower TLs (e.g. extension beyond the use of bivalves at TL2) is less well described; therefore, this has not been addressed in this project.

As discussed, throughout this project, relationships between PS-derived water concentrations and biota (particularly in higher TL organisms) is still under development. If feasible, future research initiatives may allow for the generation of models that can be used to relate EQS_{biota} to PS-derived water concentrations thereby potentially allowing for the generation of robust PS-based "trigger or threshold" concentrations that, for some compounds, could be incorporated into "tiered monitoring" approaches utilising PS.

For demonstration purposes only, such future models may incorporate steps such as those below, which are graphically illustrated in Figure 5.4:

1. EQS_{biota} threshold of TL4 back-converted to a "working" EQS_{fw} (freshwater EQS), using an appropriate TMF (see Table 5.1) and TL for mussels e.g. 2–2.1.

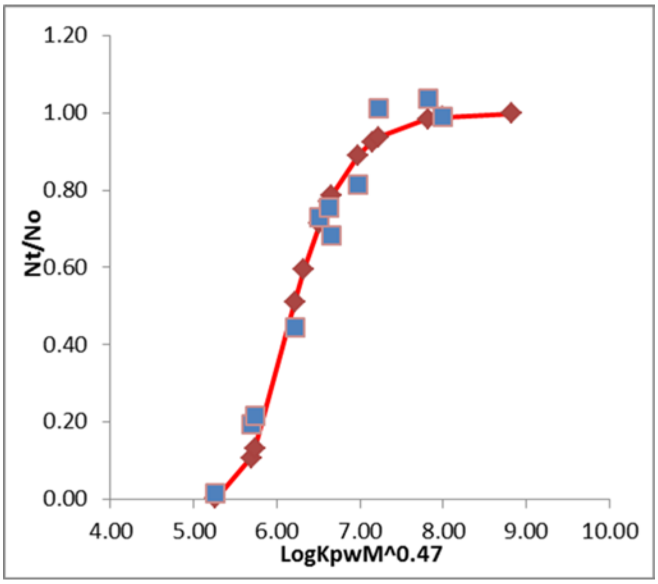

Figure 5.3. Sampling rate curve (Rs) for Poolbeg in 2014.

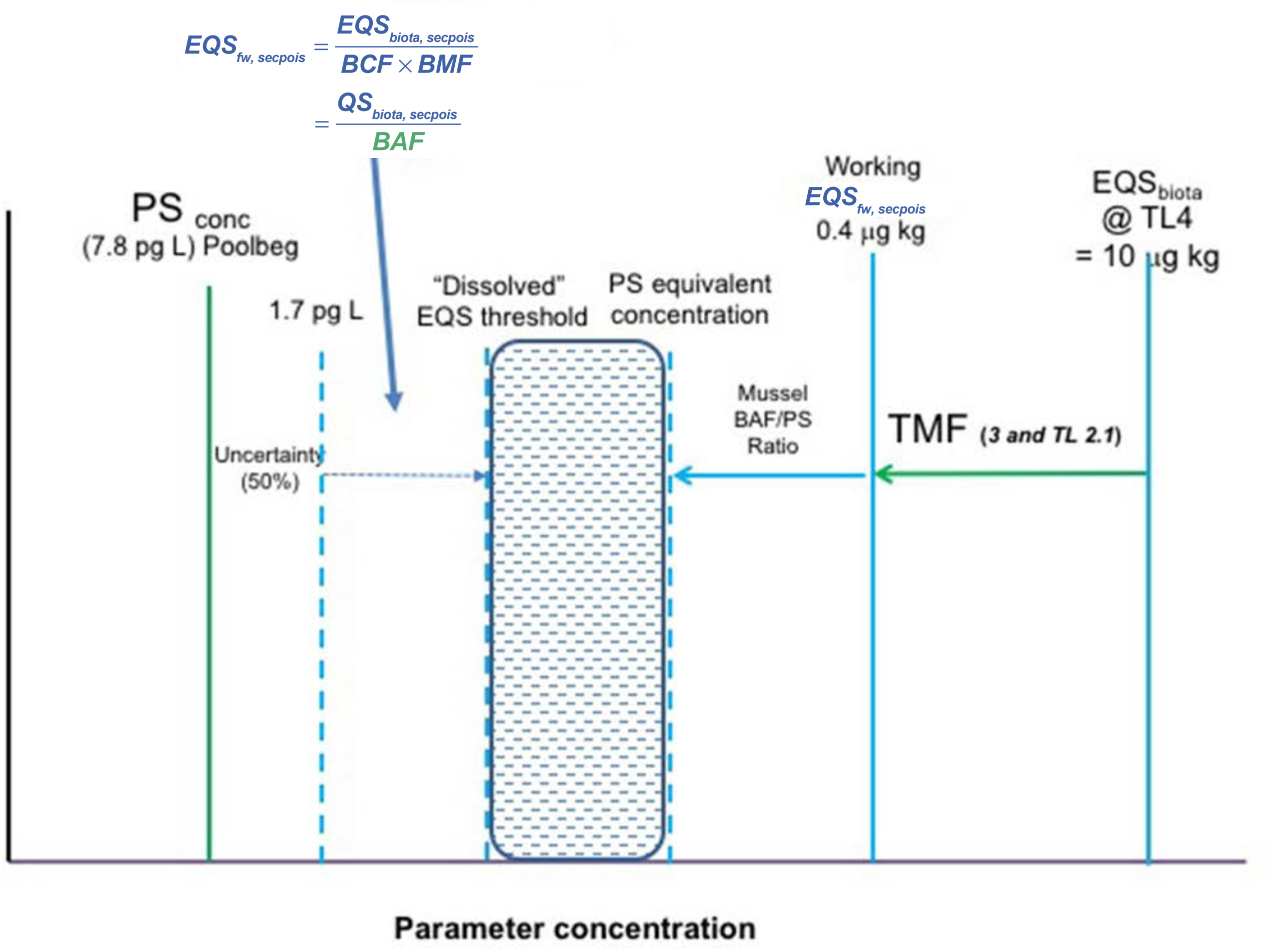

Figure 5.4. Example (HCB) to demonstrate a potential model to "back-extrapolate" EQS_{biota} to a PS threshold. $EQS_{secpois}$, environmental quality standard for secondary poisoning.

2. By further utilising this working EQS_{fw} value, it may be feasible for some compounds to use mussel BAF/PS relationships to generate a nominal "passive sampling equivalent concentration" (referred to as $PS_{conc\text{-}eq}$).
3. By using freely dissolved PS data (with associated uncertainty), it may be further feasible to convert to a "dissolved $EQS_{threshold}$" (referred to as the $EQS_{threshold}$) using "worst-case" estimates for total organic carbon and suspended solids in marine waters. This process has previously been documented by Monteyne *et al*. (2013).
4. Upon completion of each step, compound-by-compound evaluation is required to evaluate whether or not threshold generation is possible.

Table 5.1. Typical TMF values for some WFD pollutants

Substance	TMF
PBDEs	BDE47 = 1.6
Fluoranthene	Trophic dilution < 1
HCB	1.5–6
HCBD	< 1
PAHs (BaP)	Trophic dilution < 1
Dicofol	None available
PFOS	TMF 5.9
Dioxins (like compounds)	Range: TEQ-based
HBCD	1.9 (α-HBCD)

Sources of data: HBCD: OSPAR North Sea Region (2002) and Poma *et al.* (2014); HCB: Moermond and Verbruggen (2013); PBDE: Kelly *et al.* (2008); PFOS: Moermond *et al.* (2010).

BaP, benzo[*a*]pyrene.

Using the previously described relationships between PS and marine mussels (Figure 5.2), in the case of non-polar compounds it may be possible in the future to generate (marine) models capable of supporting monitoring as part of tiered approaches. Currently, such initiatives are at a research stage and highly dependent on ecosystem-specific TMF and TL data. The extension of models to higher TL organisms is currently not recommended given the range of uncertainties previously noted.

5.6 Overall Discussion, Conclusions and Recommendations

The final recommendations arising from this project are listed in Table 5.2. Significant progress has been made in recent years (and throughout the lifetime of this project) in respect of the development of mechanistic sampler–water exchange models and improved *in situ* calibration. Overall, it is generally recognised that PS undoubtedly provides a means by which low concentrations of hydrophobic pollutants (down to $\mathrm{pg\,L^{-1}}$ levels) can be measured with at least the same level of accuracy as conventional and “accepted” spot sampling methods. There is a key additional benefit that concentration information is subject to fewer biological influences, such as size and metabolism; however, it is also clear that there are still considerable challenges with regard to demonstrating the applicability of PS beyond doubt. As discussed previously, the modelling of relationships between PS concentrations and lower TL marine species (e.g. mussels) are more advanced and less complicated than those in fish and high TL species. Booij *et al.* (2006) noted that, in order for PS to further enhance its promising features, a greater level of research is needed to assess how PS measurements can best be linked to concentrations at higher levels of the aquatic food web, and that combining PS data and bioaccumulation models provides a theoretical basis for assessing and predicting bioaccumulation in biota; however, the introduction of biological (e.g. TMF, organism size and/or sex, metabolism) and spatial variables adds a high level of variability.

Table 5.3 summarises the proposed PS matrix for target analytes. There is a role for PS in both screening and trend monitoring and in feeding into “tiered” risk-based approaches to operational monitoring with future derived PS threshold values installed in an assessment hierarchy/framework where exceedance of the threshold value could be used to flag potential contamination issues.

Table 5.2. Summary of recommendations for implementation and uptake of research findings

Issue	Recommendation	Target	Time frame
Can we currently measure at the EQS?	The data collected show that many of the emerging compounds, where detected, are below EQS values. PDMS sampling allows LODs at pg L^{-1} levels, which is generally not possible with spot sampling (e.g. for PAHs).	EPA	Short–medium
With the growing number of pollutants, the cost is going to be prohibitive	While water, sediment and biota are the matrices of relevance for the WFD, with appropriate validation and for selected compounds, PS shows potential to provide at least as representative pollutant burden information as "conventional matrices".	EPA	
Can PS be employed in operational monitoring?	There is a role for PS in a risk-based screening approach to operational monitoring. The potential for the inclusion of PS as a stand-alone matrix for operational monitoring is high. The concurrent development of supporting EQS_{cw} or threshold values for some compounds may provide solutions to current (and future) ultra-trace EQS-related analytical difficulties.	EPA	
Is there a role for PS in regulatory monitoring?	PS shows potential to provide at least as representative pollutant burden information as conventional matrices. There is a role for PS in trend monitoring for certain pharmaceuticals, EDCs and non-polar organics. Using a combination of biota and PS measurements, it may theoretically be possible to derive PS thresholds. Application for PDMS samplers in offshore environments (particularly relevant for the MSFD) where biota sampling can be challenging. Working in tandem with EU guidance documentation, there is a need to develop shared monitoring tools for use at EU level. Focused, integrated multi-state research and monitoring initiatives may lead to the development of widely accepted stand-alone EQS_{cw} suitable for supporting compliance goals. It is recommended that PS could become part of a national strategy for monitoring.	Clear national strategy for the applicability of PS techniques (as part of an integrated tiered multi-agency approach) in water quality monitoring.	Medium–long
Supporting WFD and MSFD monitoring	The potential for information generated from PS to support WFD (and MSFD) monitoring is now such that there is an ongoing need to further enhance both national and international capacity-building elements in the area of PS research and development.	EPA, MI	Short–medium
Risk of missing pollution events	Evidence from this study has indicated that grab samples can miss pollution events, but longer term monitoring using PS can pick up pollutants and identify when spikes occur.	EPA	Short
PS as a useful tool for unknown environmental pollution leading to ecological impacts	There is a role for PS in both screening and trend monitoring by feeding into "tiered" risk-based approaches to operational monitoring.	EPA Irish Water	Short
Representativeness of biota	Working in tandem with EU guidance documentation, there is a need to close up biota/PS validation gaps, to work on statistical aspects of operational monitoring and to develop shared monitoring tools for use at EU level. Where biota are to be used for monitoring, it is preferable to utilise wild fish populations and/or wild/caged mussels to provide a clearer/more representative picture of water quality.	EPA EU Working Group	Medium–long
Do we have confidence in the assessment?	Through focused, integrated multi-state research and monitoring initiatives, it may be possible to provide greater validation linking PS and biota, potentially ultimately leading to the development of widely accepted stand-alone EQS_{cw} suitable for supporting compliance goals.	EPA EU Working Group	Medium–long
Is there an immediate need?	The potential for information generated from PS to support WFD (and MSFD) monitoring is now such that there is an ongoing need to further enhance both national and international capacity-building elements in the area of PS research and development.	EPA	Short

Table 5.2. Continued

Issue	Recommendation	Target	Time frame
Is PS applicable across all analytes?	Applicability must be completed on an individual parameter basis bearing in mind the applicability of PS for the compound of interest, the availability of appropriate BCF/BMF data and other ecosystem-specific factors required to improve the potential functionality of the toolkit. One important key to the likely future applicability of PS-based methodologies lies in the availability of appropriate ecosystem-specific TMF values to underpin assessment processes. The wide range of values reported in literature for individual organic compounds is a major contributor to sources of variability in completing WFD assessments. A second example of why individual parameter suitability needs to be considered lies is where EQS_{biota} have been generated based on the "sum" of congeners, e.g. of dioxins in the case of the dioxin-related compounds 2,4'-dichlorodiphenyldichloroethylene and 4,4'-dichlorodiphenyldichloroethylene. In these specific instances, individual TMF values will be required for each congener, adding further complexity to assessment processes. A final example of where specific research gaps exist is the case of PAHs, where reported TMFs range from >1 (biomagnification) to <1 (biodilution) in mussels. EQS_{biota} assessment processes (and those that include PS elements) will probably have to "err on the side of caution" when completing assessments, and each of these confounding variables will need to be considered on a parameter-by-parameter basis when making an overall assessment of model applicability.	Further research	Medium–long
How can steps be taken to evaluate suitability of PS for conventional monitoring?	There are still many knowledge gaps and caveats in relation to PS and its suitability as a tool in "compliance monitoring". However, it is evident from this work that, while additional research is required, there is scope for the development of models by which a parameter-by-parameter assessment of the suitability of PS may be completed to evaluate its suitability to support conventional monitoring.	Further research	Medium–long
How can PS be methods be improved to accelerate its adoption operationally?	Studies are required into using existing PS housings/platforms to develop materials that are more suited to polar substances in particular. POCISs, which are currently used, are not suitable for quantitative measurements and are not reliable where replicates are deployed.	Further research	Medium–long
How can PS be further demonstrated as a powerful monitoring tool?	Studies building on this project are needed whereby catchments are chosen for investigation and long-term repeated deployments are carried out to validate the PS method effectively against conventional approaches. Studies are needed that build on this initial screening project to evaluate the link between the accumulation of certain chemicals in passive samplers.	Further research	Medium–long

Table 5.3. Proposed passive sampling matrix for target analytes

Target analyte	Proposed PS matrix	Target analyte	Proposed PS matrix
Sum 7 PCBs	PDMS	Endosulphan	PDMS
Sum 14 PAHs		Cypermethrin	
Sum 6 PBDEs		Aclonifen	POCIS for trend monitoring[a]
HCBD		Bifenox	
HCB		Cybutryn	
HCHG		Dichlorvos	
HEPC		Dicofol	
OCDAN		Heptachlor/heptachlor epoxide	
HCEPC		Quinoxyfen	
TNONC		Terbutryn	
TCDAN		PFOS	
CCDAN		Diclofenac	
DDEPP		E1	
TDEPP		E2	
Dichlorvos	PDMS	EE2	
PCB			

Sum 7 PCBs: sum of 28, 52, 101, 118, 153, 138 and 180; sum 14 PAHs: sum of US-EPA 15 PAHs excluding naphthalene; sum 6 PBDEs: sum of 28, 47, 99, 100, 153 and 154.

[a] Further studies are needed to assess other passive samplers, for example Chemcatcher, or other novel materials with affinity for polar analytes. POCISs offer the potential for qualitative studies for trend monitoring but not quantitative analysis.

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Abbreviations

AA	Annual average
BAF	Bioaccumulation factor
BCF	Bioconcentration factor
BDE	Bromodiphenylether
BFR	Brominated flame retardant
BMR	Biomagnification factor
DCU	Dublin City University
E2	17-β-estradiol
EA	Environment Agency
EDC	Endocrine-disrupting compound
EE2	17-α-ethinylestradiol
EPA	Environmental Protection Agency
EQS	Environmental quality standard
$\mathbf{EQS}_{\mathbf{biota}}$	Biota EQS
$\mathbf{EQS}_{\mathbf{water}}$	Water EQS
EU	European Union
GC–MS	Gas chromatography–mass spectrometry
HBCD	Hexabromocyclododecane
HCBD	Hexachlorobutadiene
HCB	Hexachlorobenzene
IFI	Inland Fisheries Ireland
LC–MS	Liquid chromatography–mass spectrometry
LOD	Limit of detection
LOQ	Limit of quantification
MAC	Maximum allowable concentrations
MI	Marine Institute
MSFD	Marine Strategy Framework Directive
NIEA	Northern Ireland Environment Agency
NORMAN	Network of Reference Laboratories, Research Centres and Related Organisations for Monitoring of Emerging Environmental Substances
OCPs	Organochlorine pesticide
PAH	Polyaromatic hydrocarbon
PBDE	Polybrominated diphenylether
PCB	Polychlorinated biphenyl
PDMS	Polydimethylsiloxane
PFOS	Perfluorooctane sulfonic acid
POCIS	Polar organic chemical integrative sampler
PPCP	Pharmaceuticals and personal care product
PRC	Performance reference compound
PS	Passive sampling
PSD	Passive sampling device
SPE	Solid phase extraction
SPMD	Semi-permeable membrane device
TL	Trophic level
TMF	Trophic magnification factor
WFD	Water Framework Directive
WWTP	Wastewater treatment plant

AN GHNÍOMHAIREACHT UM CHAOMHNÚ COMHSHAOIL

Tá an Ghníomhaireacht um Chaomhnú Comhshaoil (GCC) freagrach as an gcomhshaol a chaomhnú agus a fheabhsú mar shócmhainn luachmhar do mhuintir na hÉireann. Táimid tiomanta do dhaoine agus don chomhshaol a chosaint ó éifeachtaí díobhálacha na radaíochta agus an truaillithe.

Is féidir obair na Gníomhaireachta a roinnt ina trí phríomhréimse:

Rialú: *Déanaimid córais éifeachtacha rialaithe agus comhlíonta comhshaoil a chur i bhfeidhm chun torthaí maithe comhshaoil a sholáthar agus chun díriú orthu siúd nach gcloíonn leis na córais sin.*

Eolas: *Soláthraímid sonraí, faisnéis agus measúnú comhshaoil atá ar ardchaighdeán, spriocdhírithe agus tráthúil chun bonn eolais a chur faoin gcinnteoireacht ar gach leibhéal.*

Tacaíocht: *Bímid ag saothrú i gcomhar le grúpaí eile chun tacú le comhshaol atá glan, táirgiúil agus cosanta go maith, agus le hiompar a chuirfidh le comhshaol inbhuanaithe.*

Ár bhFreagrachtaí

Ceadúnú

Déanaimid na gníomhaíochtaí seo a leanas a rialú ionas nach ndéanann siad dochar do shláinte an phobail ná don chomhshaol:

- saoráidí dramhaíola *(m.sh. láithreáin líonta talún, loisceoirí, stáisiúin aistrithe dramhaíola)*;
- gníomhaíochtaí tionsclaíocha ar scála mór *(m.sh. déantúsaíocht cógaisíochta, déantúsaíocht stroighne, stáisiúin chumhachta)*;
- an diantalmhaíocht *(m.sh. muca, éanlaith)*;
- úsáid shrianta agus scaoileadh rialaithe Orgánach Géinmhodhnaithe *(OGM)*;
- foinsí radaíochta ianúcháin *(m.sh. trealamh x-gha agus radaiteiripe, foinsí tionsclaíocha)*;
- áiseanna móra stórála peitril;
- scardadh dramhuisce;
- gníomhaíochtaí dumpála ar farraige.

Forfheidhmiú Náisiúnta i leith Cúrsaí Comhshaoil

- Clár náisiúnta iniúchtaí agus cigireachtaí a dhéanamh gach bliain ar shaoráidí a bhfuil ceadúnas ón nGníomhaireacht acu.
- Maoirseacht a dhéanamh ar fhreagrachtaí cosanta comhshaoil na n-údarás áitiúil.
- Caighdeán an uisce óil, arna sholáthar ag soláthraithe uisce phoiblí, a mhaoirsiú.
- Obair le húdaráis áitiúla agus le gníomhaireachtaí eile chun dul i ngleic le coireanna comhshaoil trí chomhordú a dhéanamh ar líonra forfheidhmiúcháin náisiúnta, trí dhíriú ar chiontóirí, agus trí mhaoirsiú a dhéanamh ar leasúchán.
- Cur i bhfeidhm rialachán ar nós na Rialachán um Dhramhthrealamh Leictreach agus Leictreonach (DTLL), um Shrian ar Shubstaintí Guaiseacha agus na Rialachán um rialú ar shubstaintí a ídíonn an ciseal ózóin.
- An dlí a chur orthu siúd a bhriseann dlí an chomhshaoil agus a dhéanann dochar don chomhshaol.

Bainistíocht Uisce

- Monatóireacht agus tuairisciú a dhéanamh ar cháilíocht aibhneacha, lochanna, uiscí idirchriosacha agus cósta na hÉireann, agus screamhuiscí; leibhéil uisce agus sruthanna aibhneacha a thomhas.
- Comhordú náisiúnta agus maoirsiú a dhéanamh ar an gCreat-Treoir Uisce.
- Monatóireacht agus tuairisciú a dhéanamh ar Cháilíocht an Uisce Snámha.

Monatóireacht, Anailís agus Tuairisciú ar an gComhshaol

- Monatóireacht a dhéanamh ar cháilíocht an aeir agus Treoir an AE maidir le hAer Glan don Eoraip (CAFÉ) a chur chun feidhme.
- Tuairisciú neamhspleách le cabhrú le cinnteoireacht an rialtais náisiúnta agus na n-údarás áitiúil *(m.sh. tuairisciú tréimhsiúil ar staid Chomhshaol na hÉireann agus Tuarascálacha ar Tháscairí)*.

Rialú Astaíochtaí na nGás Ceaptha Teasa in Éirinn

- Fardail agus réamh-mheastacháin na hÉireann maidir le gáis cheaptha teasa a ullmhú.
- An Treoir maidir le Trádáil Astaíochtaí a chur chun feidhme i gcomhair breis agus 100 de na táirgeoirí dé-ocsaíde carbóin is mó in Éirinn.

Taighde agus Forbairt Comhshaoil

- Taighde comhshaoil a chistiú chun brúnna a shainaithint, bonn eolais a chur faoi bheartais, agus réitigh a sholáthar i réimsí na haeráide, an uisce agus na hinbhuanaitheachta.

Measúnacht Straitéiseach Timpeallachta

- Measúnacht a dhéanamh ar thionchar pleananna agus clár beartaithe ar an gcomhshaol in Éirinn *(m.sh. mórphleananna forbartha)*.

Cosaint Raideolaíoch

- Monatóireacht a dhéanamh ar leibhéil radaíochta, measúnacht a dhéanamh ar nochtadh mhuintir na hÉireann don radaíocht ianúcháin.
- Cabhrú le pleananna náisiúnta a fhorbairt le haghaidh éigeandálaí ag eascairt as taismí núicléacha.
- Monatóireacht a dhéanamh ar fhorbairtí thar lear a bhaineann le saoráidí núicléacha agus leis an tsábháilteacht raideolaíochta.
- Sainseirbhísí cosanta ar an radaíocht a sholáthar, nó maoirsiú a dhéanamh ar sholáthar na seirbhísí sin.

Treoir, Faisnéis Inrochtana agus Oideachas

- Comhairle agus treoir a chur ar fáil d'earnáil na tionsclaíochta agus don phobal maidir le hábhair a bhaineann le caomhnú an chomhshaoil agus leis an gcosaint raideolaíoch.
- Faisnéis thráthúil ar an gcomhshaol ar a bhfuil fáil éasca a chur ar fáil chun rannpháirtíocht an phobail a spreagadh sa chinnteoireacht i ndáil leis an gcomhshaol *(m.sh. Timpeall an Tí, léarscáileanna radóin)*.
- Comhairle a chur ar fáil don Rialtas maidir le hábhair a bhaineann leis an tsábháilteacht raideolaíoch agus le cúrsaí práinnfhreagartha.
- Plean Náisiúnta Bainistíochta Dramhaíola Guaisí a fhorbairt chun dramhaíl ghuaiseach a chosc agus a bhainistiú.

Múscailt Feasachta agus Athrú Iompraíochta

- Feasacht chomhshaoil níos fearr a ghiniúint agus dul i bhfeidhm ar athrú iompraíochta dearfach trí thacú le gnóthais, le pobail agus le teaghlaigh a bheith níos éifeachtúla ar acmhainní.
- Tástáil le haghaidh radóin a chur chun cinn i dtithe agus in ionaid oibre, agus gníomhartha leasúcháin a spreagadh nuair is gá.

Bainistíocht agus struchtúr na Gníomhaireachta um Chaomhnú Comhshaoil

Tá an ghníomhaíocht á bainistiú ag Bord lánaimseartha, ar a bhfuil Ard-Stiúrthóir agus cúigear Stiúrthóirí. Déantar an obair ar fud cúig cinn d'Oifigí:

- An Oifig um Inmharthanacht Comhshaoil
- An Oifig Forfheidhmithe i leith cúrsaí Comhshaoil
- An Oifig um Fianaise is Measúnú
- Oifig um Chosaint Radaíochta agus Monatóireachta Comhshaoil
- An Oifig Cumarsáide agus Seirbhísí Corparáideacha

Tá Coiste Comhairleach ag an nGníomhaireacht le cabhrú léi. Tá dáréag comhaltaí air agus tagann siad le chéile go rialta le plé a dhéanamh ar ábhair imní agus le comhairle a chur ar an mBord.

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Role of Passive Sampling in Screening and Monitoring of New and Emerging Chemicals

Authors: Fiona Regan, Lisa Jones, Jenny Ronan,
Denis Crowley, Evin McGovern and Brendan McHugh

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Climate - Water - Sustainability
Identifying pressures • Informing policy • Developing solutions

Identifying pressures

The aquatic environment – including lakes, rivers, ground water, estuaries and coastal zones – is vulnerable to changes caused by human activities. Accurately monitoring the status of water bodies under the EU Water Framework Directive (WFD) poses a huge challenge. One major difficulty is gathering representative information on levels of chemical contamination.

This project focused primarily on developing the capacity for using passive sampling in Ireland by exploring its applicability in relation to WFD requirements, and by documenting potential roles for passive sampling in Irish waters. Water and biota samples from 19 locations in five counties (Donegal, Mayo, Galway, Cork and Dublin) were taken, and passive samplers were deployed over three years. In Dublin and Cork, studies were carried out over two years to assess changes in chemical contamination over time. Analytical methods for pesticides, pharmaceuticals and non-polar organics were adapted for application to water, biota and passive sampler extracts.

Informing policy

Annex X to the WFD lists priority hazardous substances, a list that was updated and expanded in Directive 2013/39/EU to identify a number of emerging chemicals of concern, including some pesticides and biocides, industrial chemicals and endocrine disruptors. Although Member States can monitor priority substances in 'whole' water, biota or sediment, the environmental quality standards (EQSs) are primarily set for the water phase, as annual average and maximum allowable concentrations, although biota EQS have been established for 11 substances. This research suggests that passive sampling has more evident applicability in the marine environment, specifically in trend and offshore monitoring supporting both the tiered approach and the Marine Strategy Framework Directive (MSFD). In a wider context, as the biota EQS embrace other protection goals, such as protection of aquatic life, it is clear that passive sampling can still play a significant role in WFD monitoring. This project proposes a "framework tiered" approach that works with legislative requirements to capitalise on the strengths of passive sampling in monitoring WFD requirements.

Developing solutions

The research findings suggest that it is theoretically possible to use passive sampling to screen for and measure the vast majority of organic compounds. However, several conditions must be met before passive sampling techniques can be considered fully suitable for routine monitoring. Their application for WFD purposes requires additional performance criteria. These include the calculation of accurate uptake rates to calculate time-weighted average contaminant concentrations in water, as well as strict protocols for in situ deployment.

There is a need for further discussion on a clear national strategy for applying passive sampling techniques as part of a tiered approach to water quality monitoring. A significant number of questions relating to the balance between scientific and practical considerations remain to be addressed. Ultimately, there is a need for consistency and comparability among Member States in the assessment of WFD compliance.

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