Passive sampling of polar emerging contaminants in Irish catchments

Lisa Jones, Jenny Ronan, Brendan McHugh and Fiona Regan

ABSTRACT

Passive sampling (PS) is a very useful approach for the monitoring of emerging contaminants in environmental matrices, showing greater sensitivity than can be achieved by current best practice – grab sampling – and is applicable to a wide variety of compounds. An EU Directive (2013/39/EC) has added substances to the existing Water Framework Directive (WFD) Priority Substance list. Investigation into PS in the monitoring of these compounds is necessary to show the potential of this technique in supporting monitoring requirements under the WFD. A catchment-based approach evaluated the occurrence of these compounds in Irish surface waters. This work deals with the challenges associated with the use of PS in a legislative context, and for routine monitoring of emerging contaminants. Looking at a number of sites across Ireland, upstream and downstream of wastewater treatment plants, the focus was on polar analytes and polar PS (POCIS). With method limits of detection (LODs) of 0.001 mg L^{-1} pharmaceuticals and endocrine disrupting chemicals (EDCs) were found in water and passive samples alike, whereas the polar pesticides were not often detected or were below the annual average environmental quality standard levels. The results of this study show the potential for PS as a monitoring technique for emerging and watch-list chemicals.

Key words | catchment, EDCs, passive sampling, pharmaceuticals, polar compounds, water quality

Lisa Jones
Fiona Regan (corresponding author)
School of Chemical Sciences and Water Institute,
Dublin City University,
Dublin,
Ireland
E-mail: *fiona.regan@dcu.ie*

Jenny Ronan
Brendan McHugh
Marine Institute,
Rinville, Galway,
Ireland

INTRODUCTION

Passive sampling (PS) techniques are rapidly developing as very cost-effective state of the art tools to identify and measure 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, several questions remain regarding the merits of PS in providing representative sampling of chemicals in environmental waters, the quantification of water column pollutant loadings and its suitability for adoption for checking legislative compliance.

PS is also a valuable tool owing to the ability to sample large volumes of water, the ease of deployment and processing compared with water or biota sampling and the non-mechanical operation meaning no external power input is required (Harman *et al.* 2012). PS have the ability to measure the freely dissolved fraction, 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 directly applies to risk assessment as the freely dissolved fraction is proportional to the chemical activity of the compound (Harman *et al.* 2009; Booij *et al.* 2016). One important consideration is that passive samplers can provide more representative information than infrequent spot sampling on the occurrence of pollutants in water bodies, particularly where concentrations fluctuate markedly in time.

It is theoretically possible to use passive sampling 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 as fully suitable for the purposes of routine monitoring. Their application for Water Framework Directive (WFD) (2000/60/EC) (European Parliament 2000) purposes requires additional performance criteria. These include the calculation of accurate uptake rates in order to calculate time weighted average (TWA) contaminant concentrations in water, and strict protocols for *in situ* deployment. The authors have previously provided a full summary of a role for passive sampling in supporting WFD compliance and monitoring (Jones *et al.* 2015).

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Passive sampling is a diffusion-based technique, with samplers consisting of a material with a high affinity for the analytes of interest. In some samplers (e.g. low density polyethylene strips and silicone rubber sheets), this receiving phase can be bare, while in other samplers (e.g. polar organic chemical integrative sampler (POCIS)), it is separated from the sampling medium (water) by a diffusion limiting membrane. Different combinations of membrane and receiving phase allow the sampling device to be tailored for various purposes (Booij & Smedes 2010; Smedes *et al.* 2010; Jones *et al.* 2015). As a high affinity for pollutants of interest is selected for the receiving phase, it achieves a higher concentration within the sampler compared with that in the water phase and can provide significant improvements in analytical detection limits. There are the two fundamentally different modes of uptake by receiving phases, absorption (in partition samplers such as polydimethylsiloxane (PDMS)), and adsorption when target compounds form strong bonds to the sampling material (e.g. POCIS) (Booij & Smedes 2010; Smedes *et al.* 2010; Jones *et al.* 2015). Uptake of pollutants by adsorption-based 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 (Booij & Smedes 2010; Smedes *et al.* 2010; Jones *et al.* 2015). Passive samplers such as the POCIS are often used as alternative sampling methods for EDCs as they can provide time-integrated trace levels of pollutants in water and have been suggested as complementary methods for WFD surveillance, operational and investigative monitoring (European Commission 2009). Sampling rates for these *in situ* devices which can consider all environmental factors are not yet viable, thus POCIS is generally applicable for use as a qualitative/screening device (Figure 1).

The primary aim of this study 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 Marine Strategy Framework Directive (MSFD) (European Parliament and Council of the European Union 2008). In Dublin and Cork catchments, studies were carried out over two years to assess based variations in chemical contamination. Analytical methods for pesticides, pharmaceutical and non-polar organics were adapted and developed for application to water, and passive sampler extracts.

The study includes oestrogens, oestrone (E1) and 17β oestradiol (E2), the synthetic oestrogen 17α-ethynylestradiol (EE2) and diclofenac. This is because an increasing volume of scientific data indicates potential negative effects of steroid oestrogens at European Union (EU) level, to or via the aquatic environment. There is also a threat posed to the environment by the occurrence of pharmaceuticals and personal care products (PPCPs) (Snyder *et al.* 2009; Wilkinson *et al.* 2017). The main source of PPCPs is through the wastewater management systems present in all major urbanised areas (Zhang *et al.* 2008; Cabeza *et al.* 2012; Bu *et al.* 2013). The use of wastewater treatment plants (WWTPs) serves as a means for the removal of organic matter and other substances prior to discharge into the environment, although not all the compounds contained within the effluent can be removed or degraded to a harmless product. The increased

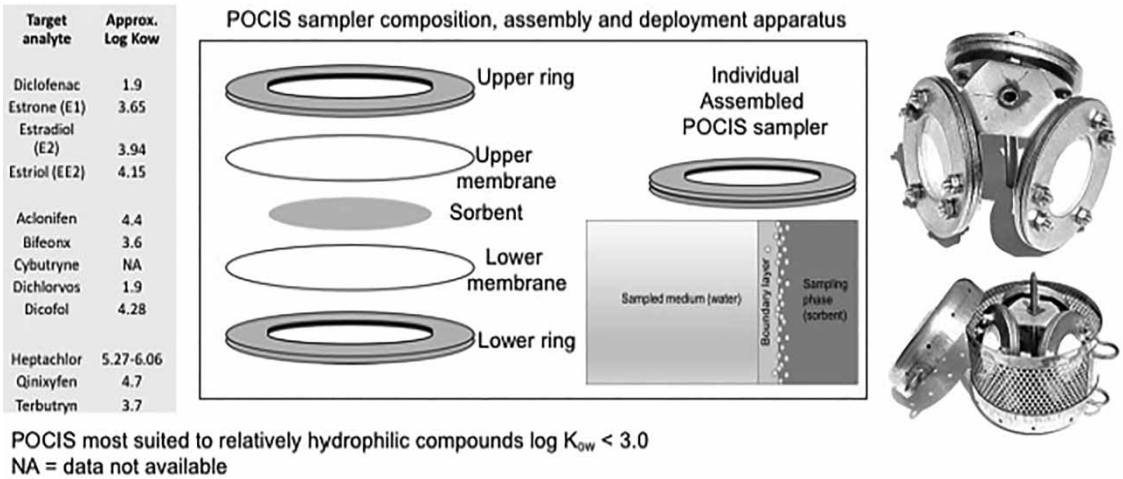

Figure 1 | Schematic illustrating components of the POCIS sampler, the mechanism of analyte interactions and the deployment apparatus used for multiple samplers. The samplers are used for polar analytes, the K_{ow} are shown in the table.

construction of WWTPs, under EU regulations, has partly removed the discharge of raw sewerage into the environment. The ingestion of pharmaceuticals and the metabolism (or lack of) and their subsequent excretion (generally via urine and faeces) serves as a major route to the environment. The objective of this part of the study was to screen a number of samples associated with WWTP runoff for pharmaceuticals and steroids, and to assess the value of passive sampling in monitoring these compounds.

These concerns have resulted in the inclusion of E1, E2 and EE2 in the EU watch list of substances for Union-wide monitoring (European Commission 2015), whereupon it is anticipated this will generate high-quality data on their concentrations in the aquatic environment for the purpose of supporting future prioritisation exercises. Under this legislation maximum method detection limits of 0.4 ng L^{-1} for E1 and E2 and 0.035 ng L^{-1} for EE2 on a total water basis have been set. It is generally recognised that there are a number of difficulties in reaching such low detection limits using traditional spot water sampling and marine strategy (MS) methods due to the low instrument sensitivities required, volumes of water required, increased dilution effects and representative sampling in what is generally a dynamic environment.

Pesticides and biocidal products comprise the majority of the emerging compounds (nine) most recently added to EU water legislation (2013/39/EU). These compounds are the focus of the second part of the study. This case study focussed on aclonifen, bifenox, dicofol, quinoxyfen, cybutryne, dichlorvos and terbutryn.

Aclonifen (2-chloro-6-nitro-3-phenoxyaniline) is a diphenyl-ether (DPE) herbicide used in the pre-emergence control of broad-leaved and grass weeds (Directive 2011a; Loos 2012a). Bifenox is a selective herbicide used in control of annual broad-leaved weeds and some grasses in numerous crops, e.g. in cereals, maize, soya beans, rice and other crops (Directive 2011b; Loos 2012a, 2012b). Cybutryne (Irgarol) is an effective triazine herbicidal biocide (or algicide) mainly used as an antifouling agent in paints for boats and vessels. It is applied at marine as well as at inland freshwater sites (Manzo *et al.* 2006; Loos 2012a, 2012b). Dicofol is an organochlorine pesticide (arcaricide; miticide) that is chemically related to dichlorodiphenyltrichloroethane (DDT), and used for controlling mites that damage cotton, fruit trees and vegetables (Hoekstra *et al.* 2006; Fujii *et al.* 2011; Loos 2012a, 2012b). Heptachlor is an insecticide which is banned and is no longer used in the EU. Heptachlor-epoxide is its degradation product (Directive 2011c; Loos 2012a, 2012b). Quinoxyfen is a fungicide often used to control powdery mildew infections on grapes and hops (Cabras *et al.* 2000; California Department of Pesticide Regulation 2004; Loos 2012a, 2012b). Until now, limited work has been published which included all of these compounds in relation to surface water occurrence. Analysis of these compounds is problematic, requiring a range of specific methods and strict protocols. This study involved collection of passive and grab samples in a catchment and monitoring these compounds for two periods (summers 2014 and 2015).

MATERIALS AND METHODS

Site selection

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 deployments, options for use of structures for deployment, restrictions on deployment of moorings and tidal range in transitional and coastal waters. Locations of the sites selected, and types of sample collected at each site are outlined in Table 1.

In order to evaluate the benefit of the catchment approach to identify point sources and pathways of pollution, the River Lee catchment in Cork was selected for the study of potential impact from the natural oestrogens, oestrone (E1) and 17β oestradiol (E2) and the synthetic oestrogen 17α ethynylestradiol (EE2). The river Lee flows from an area of low anthropogenic activity, through agricultural land to Cork City entering the Celtic Sea via the industrialised Cork Harbour (100 km^2 surface). Within the study area, Lough Mahon and the River Lee in Co. Cork received a poor WFD classification status for fish. Evidence of pollutant stress in mussels has also been revealed by scope for growth measurements, potentially due to

Table 1 | Overview of sampling and rationale from this study (Figure 2)

County	Site	Rationale	POCIS	Water
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	✓	✓

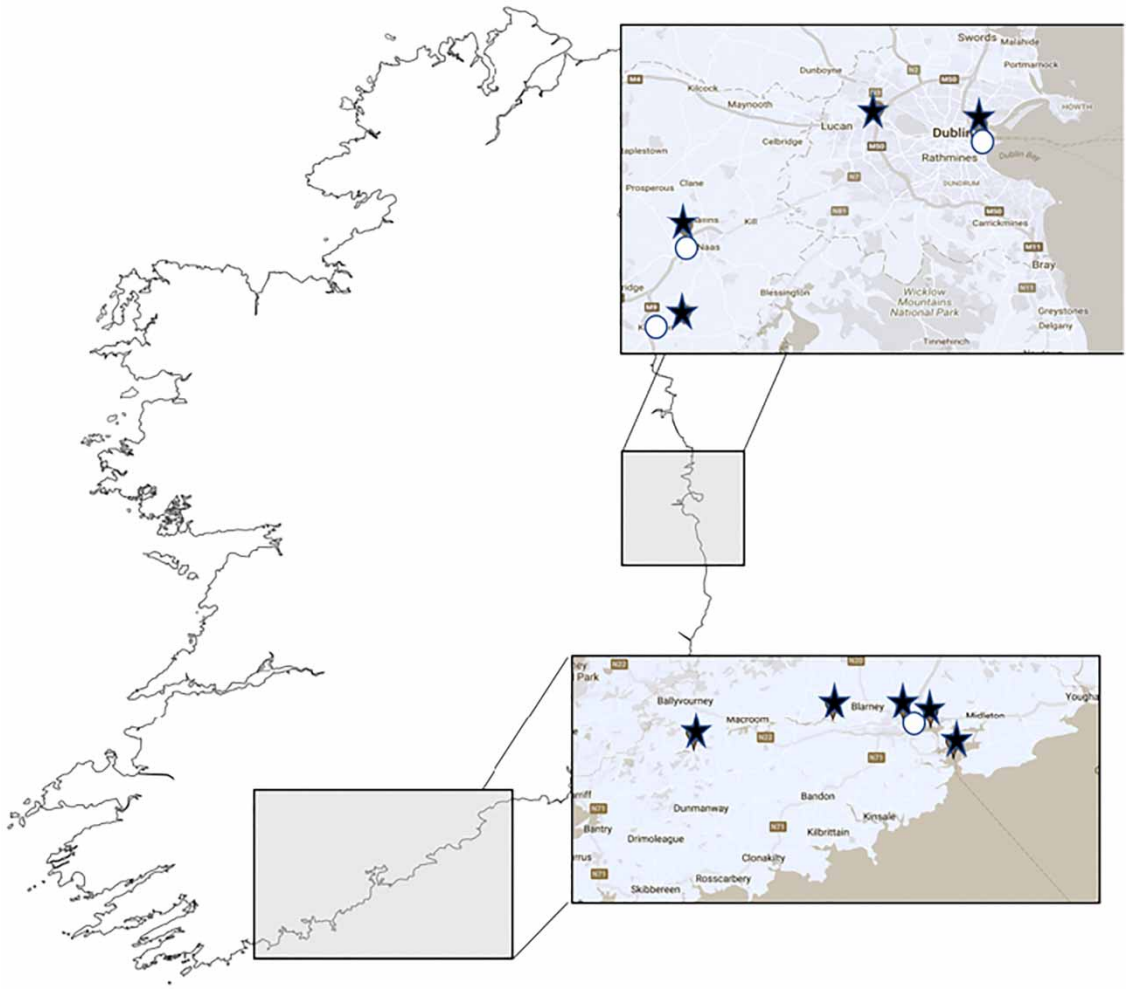

Figure 2 | Map of Ireland with two inserts highlighting Dublin catchment (top), and Cork catchment (bottom). Sampling sites are marked in stars. WWTPs are marked with circles.

untreated wastewater from population centres such as Cork City. Secondary treated waste enters Cork Harbour from Cork City (333,000PE) and from a number of other potential inputs ranging including industrial waste and riverine inputs of agricultural run-off and untreated waste from the River Lee catchment.

In Dublin, the river Liffey is one of the most important rivers in Ireland and is a major water source for the Greater Dublin Area. The Liffey has been a controlled river for more than 50 years. It is dammed at Pollaphuca and Leixlip and there are also three hydro-electric power stations along its course. Due to this artificially controlled hydraulic regime, the Liffey is defined as a 'Heavily Modified Water Body' under the Water Framework Directive (Parliament 2000). The water quality Q-rating in the Liffey varies along its length between 5 (close to source) and 2–3 in the lower reaches (close to sea). The Eastern River Basin Management Plan categorises the Liffey as of 'moderate' quality throughout the majority of its course (Dublin City Council 2015). The river is designated in parts under the Urban Waste Water Treatment Regulations 2001, as a 'sensitive' river (downstream of the Osberstown sewage treatment works to Leixlip Reservoir, County Kildare) (European Parliament 2004). The WFD characterisation process has identified WWTP as primary pressures on the Liffey system.

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 gas chromatography–mass spectrometry (GC-MS) depending on compounds analysed.

Water extraction for pesticides

The sample was passed through a styrene di-vinyl benzene polymer solid phase extraction (SPE). The cartridge was washed, dried and the steroids desorbed with dichloromethane. This extract was evaporated to incipient dryness and dissolved in a 90:10 v/v% iso-hexane:propan-2-ol mixture and cleaned-up using normal phase chromatography with an Amino LC column fractionation. The resulting extract was again evaporated to incipient dryness before being dissolved in 50% aqueous CH_3OH. This extract was then fractioned using reverse phase chromatography with a standard C18 phase column. The resulting extract was evaporated to incipient dryness and dissolved in 10% aqueous CH_3OH. 100 μL of this was analysed using high performance liquid chromatography with negative ion atmospheric photo-ionisation interface and time of flight mass spectrometric detection.

Water extraction for pharmaceuticals and EDCs

Water samples (5 L) were extracted as per Ronan & McHugh 2013). Briefly, samples were filtered with 0.45 μm glass fibre filters prior to SPE. 5 L water samples were filtered with 0.45 μm glass fibre filters (Whatman GF-F, General Electric company, USA). Sample clean-up was conducted using Oasis hydrophilic-lipophilic-balanced (HLB) 3 mL, 60 mg SPE cartridges (Waters, Milford, MA, USA). Bakerbond SPE™ 75 mL reservoirs (JT Baker, Avantor Performance Materials, Centre Valley, PA, USA) were attached to the SPE cartridges to enable application of the sample. Cartridges were rinsed and conditioned with 3 mL pestiscan grade CH_3OH and deionised water, prior to addition of the sample extract. Cartridges were rinsed with 3 mL 5% CH_3OH in deionised H_2O, and samples were eluted in 2 mL CH_3OH under a gentle vacuum. The sample was then reduced to dryness under nitrogen at 35 °C and re-suspended in 130 μL of 1:4 CH_3OH: water. 10 ng of external standard warfarin (Sigma Aldrich, St Louis, MO, USA) was added. 20 μL of this solution was injected into the high performance liquid chromatography (HPLC) system.

Passive samplers

POCIS devices used in this study were as developed by Alvarez *et al.* 2004 (Alvarez *et al.* 2004) and were supplied by the National Laboratory Service (NLS), Environment Agency, United Kingdom. They consisted of a layer of Oasis HLB sorbent (230 mg approximately, Waters, Milford, MA, USA) sandwiched between two membrane layers of polyethersulphone polymer, fixed in place by two circular steel rings secured with stainless steel nuts and bolts. Each POCIS disc was mounted on holders (three per sampler) and placed inside a protective perforated stainless-steel housing. A POCIS device (three POCIS discs) and one single POCIS disc for use as a field blank were stored in an airtight metal canister at −30 °C and transported to the site in cold conditions. POCIS devices were deployed at 1 m depth at selected sites for a period of one month. The field blank was exposed to the environment during deployment and retrieval. Storage and transportation of the devices was conducted in a manner that would not expose them to contamination. Samplers and field blanks were stored at −30 °C prior to transport (in cold conditions) to the NLS, UK for extraction and analysis.

Passive sampler extracts were analysed as per the Environment Agency (UK) Blue Book 220, method B. On arrival to the laboratory the POCIS discs were cleaned to remove any debris or stubborn deposits. Any excess water was removed where necessary with absorbent tissue and the discs allowed to air-dry overnight. The loaded POCIS was carefully dismantled and the sorbent transferred with CH_3OH into a glass chromatography column fitted with a glass wool plug and a stopcock. The CH_3OH used to rinse the sorbent into the column was collected to be pooled with the SPE eluent. The sample was eluted with 40 mL CH_3OH (adjusted to near dropwise flow). The collected eluate and rinse was evaporated using rotary evaporation to approximately 1 mL.

A schematic illustrating this approach is shown in Figure 3.

Analysis for pharmaceuticals and EDCs

The HPLC system consisted of an Agilent 1200 Series Game Pad, Agilent 1200 Binary Pumps, an Agilent 1200 High Performance Autosampler and an Agilent 1200 thermostatted column compartment (Agilent Technologies Deutschland GmbH, Böblingen, Germany). A Kinetex 4.6 × 50 mm, 2.1 mm ID C18 2.5 μm particle size column (Phenomenex, Macclesfield, Cheshire, UK) was used for chromatographic separation. For LC-MS/MS experiments, an Applied Biosystems 3200 Q-TRAP was used (Applied Biosystems, Foster City, CA, USA). The mobile phases were 0.025% TEA (triethylamine) in deionised water (A) and 0.025% TEA in 5:95 water: acetonitrile (B) flowing at 300 μL per minute with a gradient as follows: 0 to 2 min (5 to 31.5% B), 2 to 7 min (31.5 to 34% B), 7 to 9 min (100% B) and 9 to 12 min (5% B). The ESI source (Turbo-Ionspray,

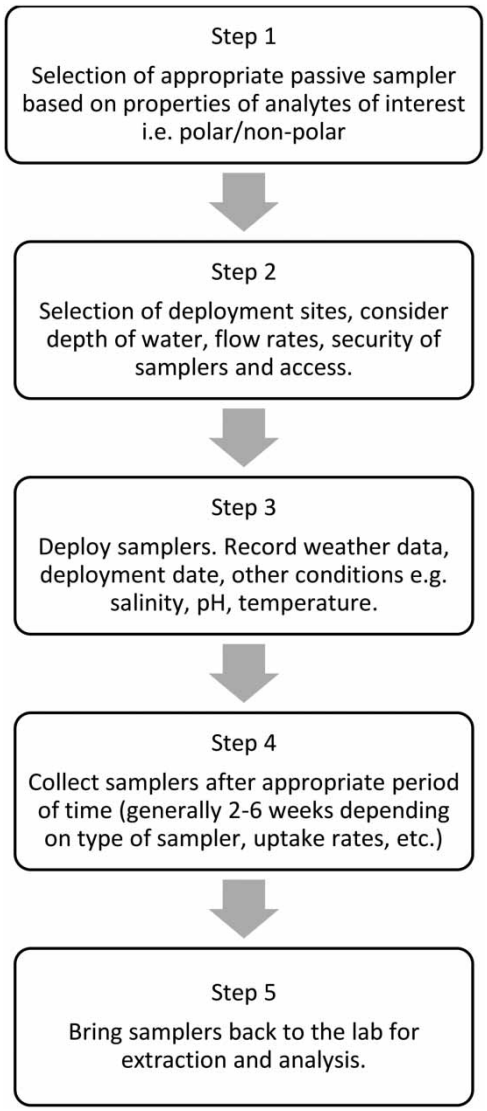

Figure 3 | Basic schematic showing the steps involved in the monitoring approach using passive sampling.

Applied Biosystems) was operated in negative mode at 550 °C and −4,400 V. Quantification was performed using matrix-matched standards for mussel tissue, and aqueous standards for water samples.

Analysis for pesticides

The HPLC system consisted of an Agilent 1100 Series Game Pad, Agilent 1100 Binary Pumps, an Agilent 1100 High Performance Autosampler and an Agilent 1100 thermostatted column compartment (Agilent Technologies Deutschland GmbH, Böblingen, Germany). A Luna phenyl hexyl 2 × 150 mm, 3 μm particle size column (Phenomenex, Macclesfield, Cheshire, UK) fitted with a Luna phenyl propyl 4 × 2 mm guard column was thermostatted at 60 °C was used for chromatographic separation. For HPLC-MS/MS experiments, an Applied Biosystems 3200 Q-TRAP was used (Applied Biosystems, Foster City, CA, USA). The mobile phases were deionised water (A) and 0.025% TEA in 95:5 CH_3OH: acetone (B) flowing at 300 μL per minute with a gradient as follows: 0 to 0.5 min (5 to 20% B), 0.5 to 1 min (20 to 40% B), 1 to 12 min (40 to 80% B), 12 to 14 min (80% B) and 14 to 14.5 min (80 to 5% B) with analysis as per the Environment Agency Blue Book 220.

RESULTS AND DISCUSSION

This is the first time that pharmaceuticals are being proposed for addition to existing European water legislation and very low environmental quality standards (EQS) values (and 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 estrogenic hormones and is a key intermediate in industrial synthesis of other estrogens and of various hormonal 19-norsteroids.

From the results presented in Table 2, it can be seen that pharmaceutical compounds were detected in both water and passive samplers collected in 2014 and 2015. As accurate sampling rates for POCIS were not available, levels are presented as ng/device for the particle size distributions (PSDs) for diclofenac and as estimated 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 determinations as measured in both the passive sampling devices 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) 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 E2 was often detected when E2 and EE2 were not. The 5 L ($n = 3$) grab samples collected at each sampling point allowed the achievement of a low limit of quantitation (LOQ) (method LOQ of 0.001 mg L^{-1}).

Table 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

	Matrix	Kilcullen	Osberstown	Lucan	Poolbeg
Analyte		**2014**			
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 (17.1)	<0.06 (14.6)	<0.06 (12.2)	0.05 (9.8)
EE2		<0.06 (17.1)	<0.06 (14.6)	<0.06 (12.2)	<0.04 (7.8)
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
Analyte		**2015**			
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 (17.1)	<0.06 (14.0)	0.06 (11.1)	0.07 (13.0)
EE2		<0.06 (17.1)	<0.06 (14.0)	<0.06 (11.1)	<0.06 (11.1)
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 (17.1)	<0.06 (14.0)	0.06 (11.1)	0.07 (13.0)
EE2		<0.06 (17.1)	<0.06 (14.0)	<0.06 (11.1)	<0.06 (11.1)

Concentrations of diclofenac (Dcl) in POCIS presented as amount (ng/device) while E1, E2 and EE2 in POCIS is estimated based on sampling rates. Other results in ng L^{-1}. nd = not detected.

Steroid estrogen data from spot water sample and POCIS data available for samples collected between 2013 and 2014 from the River Lee catchment are presented in Table 3. Sites were assessed on a catchment basis and include freshwater and estuarine/marine samples. Five sampling points in the Lee catchment in County Cork were sampled once each in 2013 and 2014. E2 and EE2 were not detected in water samples in 2013 and 2014. E1 was added to the suite of compounds in 2014 and was detected in Lough Mahon and the Outer Harbour at similar concentrations as those calculated in POCIS. E1 was also detected in water at Iniscarra and in POCIS in Iniscarra and Shandon. Concentrations of E2 in POCIS were higher in 2013, with a surprising spike of EE2 detected in Iniscarra, a remote upstream site (1.39 ng L^{-1}).

From the results of this work, the currently unreliable nature of polar passive sampling was explored, as grab samples often detected estrogenic events that were missed by the passive samplers. A 2016 interlaboratory study (ILS) found that for most polar compounds both the analytical variability and the variability of applied calibration data contributed similarly to the overall variability of water concentration estimates. The same study also found the exchange of polar compounds between sampler and the aqueous phase was often observed to be anisotropic and therefore generally not possible to use release of PRCs to calibrate the uptake rate for calculation of TWA water concentrations (Vrana *et al.* 2016). This result could be combatted through the deployment of more PSDs, multiple PSDs at each site and flow data collected to allow for more accurate sampling rates to be calculated. The current study does not demonstrate any advantages of polar passive sampling for pharmaceuticals and EDCs outside of screening potential. This is reflected in a recent position paper arising from a NORMAN network-supported workshop in Lyon (France) in November 2014 (Miège *et al.* 2015).

Results of this work are presented in Tables 2–5, showing data for 2014 and 2015 in Dublin and for 2013 and 2014 in Cork catchments. Targeted pesticides were not detected in many cases and were otherwise present in concentrations below the annual average environmental quality standard (AA EQS). The analytes were detected using passive samplers in 2014 in Dublin at Kilcullen, but these were absent in 2015. The results from the passive samplers allowed for the assessment of pharmaceutical concentrations where large enough grab samples were not feasible. The benefits of this technique are counted as the ease of use and deployment, the selectivity and the ability to sample large volumes of water.

Table 3 | Concentrations of pharmaceuticals and EDCs along the Lee catchment in water and passive samples collected in 2013 and 2014

	Matrix	Inchigeelagh	Iniscarra	Shandon	Lough Mahon	Outer Harbour
Analyte		**2013**				
Dcl*	POCIS	na	na	na	na	na
E2		<0.5	<0.5	<0.5	2.36	1.98
EE2		<0.2	1.39	<0.2	<0.2	<0.2
Dcl	Water	7.2	3.5	4.5	7.8	2.8
E2		nd	nd	nd	nd	nd
EE2		nd	nd	nd	nd	nd
Analyte		**2014**				
Dcl*	POCIS	<0.1	0.14	0.92	0.75	0.27
E1		<0.51	0.24	0.37	0.48	0.37
E2		<0.13	<0.04	<0.04	0.06	0.09
EE2		<0.12	<0.04	<0.04	<0.04	0.07
Dcl	Water	9.7	12.7	6.2	8.7	4.3
E1		nd	0.41	nd	0.41	0.54
E2		nd	nd	nd	nd	nd
EE2		nd	nd	nd	nd	nd

Results in ng L^{-1}. nd = not detected, na = not analysed. Sites are listed from upstream to downstream (left to right).

From the results of this work the currently unreliable nature of polar passive sampling was explored as grab samples often detected estrogenic events that were missed by the passive samplers. A 2016 ILS found that for most polar compounds both the analytical variability and the variability of applied calibration data contributed similarly to the overall variability of water concentration estimates. The same study also found the exchange of polar compounds between sampler and the aqueous phase was often observed to be anisotropic and therefore generally not possible to use release of PRCs to calibrate the uptake rate for calculation of TWA water concentrations (Vrana *et al.* 2016). This result could be combatted through the deployment of more PSDs, multiple PSDs at each site and flow data collected to allow for more accurate sampling rates to be calculated. The current study does not demonstrate any advantages of polar passive sampling for pharmaceuticals and EDCs outside of screening potential. This is reflected in a recent position paper arising from a NORMAN network-supported workshop in Lyon (France) in November 2014 (Miège *et al.* 2015).

As these compounds have only recently been included in the proposed legislation, there is little information on widespread occurrence and background levels across Europe. However, some studies have reported the determination of these compounds in relation to WWTP inputs. Diclofenac is a widely used non-steroidal anti-inflammatory and antipyretic drug mainly administered via the oral route. It is rapidly absorbed in the body. Un-metabolised or partially excreted diclofenac is known to be mainly resistant to biological wastewater treatment and reaches the water cycle (Xiao *et al.* 2015). In 1998, diclofenac was detected in rivers and lakes in Switzerland with the data strongly suggesting input from human medical use via WWTPs. Levels detected were in the high ng L^{-1} level, much higher than the results from the River Liffey (Buser *et al.* 1998). A study carried out in Berlin in 2000 found levels of diclofenac in concentrations from n.d – 1,030 ng L^{-1} in surface water samples downstream from WWTP and sewage treatment plants (STPs) (Heberer *et al.* 2002). Looking at pharmaceutical residues in STP effluents from France, Greece, Italy, Sweden, Germany, the UK and Canada (n = 65), a review in 2005 reported concentrations of diclofenac from n.d. to 0.81 μg L^{-1} (Petrović *et al.* 2005). A further study in France reported the following levels of diclofenac in various matrices: 0.9 ng L^{-1} (tap water), 0.7 ng L^{-1} (surface water), 2.6 ng L^{-1} (marine water) and 9 ng/500 mL (wastewater). This is comparable with the results from this study. They also collected samples in the Hérault watershed and detected diclofenac in levels of 1.36–33.2 ng L^{-1}, higher than levels found in the Liffey (Togola & Budzinski 2008). In 2008, a review reported that diclofenac is ineffectively removed by WWTPs, with removal efficiency varying from 0% to 80% depending on the operation conditions of the

Table 4 | Concentrations of pesticides in passive samplers (ng/device) and in water (ng mL^{-1}) in the Dublin catchment sites.

	Matrix	AA EQS	Kilcullen	Osberstown	Lucan	Poolbeg
Analyte			2014			
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
Analyte			2015			
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

nd = not detected. Detection limits for aclonifen, bifenox, cybutryn, dichlorvos, dicofol, heptachlor/heptachlor epoxide, quinoxyfen, terbutryn = 0.5–5.0 ng mL^{-1}. AA EQS – annual average environmental quality standard.

WWTPs (Zhang *et al.* 2008). A study from 2014 found levels of diclofenac in WWTPs in Greece ($n = 32$) to range from n.d. to 5,164 ng L^{-1} (Kosma *et al.* 2014). Another recent study looking at seawater concentrations of NSAIDs in Portugal found diclofenac to occur from n.d. to 30 ng L^{-1} ($n = 5$) (Paíga *et al.* 2015). A study reported diclofenac levels of 46–1,171 ng L^{-1} (WWTP effluent; $n = 4$) and <LOD (river water; $n = 1$). The same study also reported POCIS TWA levels of diclofenac to be 0.39 ng L^{-1} in river water and 0.25 ng L^{-1} in tap water (Tanwar *et al.* 2015).

Discharge from STP or WWTP, as well as direct introduction via excretion by livestock, represent major sources

Table 5 | Concentrations of pesticides in passive samplers (ng/device) and in water (ng L^{-1}) in the Cork catchment sites

	Matrix		Inchigeelagh	Iniscarra	Shandon	Outer Harbour	Lough Mahon
Analyte			2013				
Aclonifen	Water (ng L^{-1})	120	nd	nd	nd	nd	nd
Bifenox		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
Analyte			2014				
Aclonifen	POCIS (ng/device)		nd	nd	nd	nd	nd
Bifenox			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 (ng L^{-1})	120	nd	nd	nd	nd	nd
Bifenox		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

nd = not detected. Detection limits for aclonifen, bifenox, cybutryn, dichlorvos, dicofol, heptachlor/heptachlor epoxide, quinoxyfen, terbutryn = 0.5–5.0 ng mL^{-1}.

of estrogenic compounds to surface water. This is particularly relevant as the upstream sampling sites in this study are located in agricultural areas. Information on steroid hormones in the environment is comparatively less available than diclofenac. Occurrence and concentration of hormones in effluent, freshwater and groundwater varies in different countries. A recent review reported on the occurrence and concentration of hormones found in effluent, freshwater and groundwater in different countries. This report showed that in the effluent of WWTP and STP, the concentrations of estrogenic compounds usually are below 50 ng L^{-1}, but there are unexpected high concentrations of estriol and 17α-estradiol about 590 ng L^{-1} and 180 ng L^{-1}, respectively, found in America (Li *et al.* 2014). A review in 2011 summarised that the concentrations of hormones in influent and effluent are generally quite similar, indicating that the elimination of hormones is incomplete or that the compounds are resistant to typical wastewater treatment processes (Pereira *et al.* 2011). A study in Turkey found the following levels of hormones in surface waters ($n = 6$): E1 (n.d.–6.04 ng L^{-1}) with a percentage occurrence of 0–40%; E2 (n.d.–10.2 ng L^{-1}) with a percentage occurrence of 20–80%; EE2 (n.d.–14 ng L^{-1}) with a percentage occurrence of 0–40% (Aydin & Talinli 2013).

This is the first report of a catchment-based assessment of pharmaceuticals in Ireland. As a result of their growing use, pharmaceuticals have been found in aquatic systems, in STP effluents, surface waters and even drinking waters. Although the quantities of pharmaceuticals and their bioactive metabolites being introduced into the environment is likely low, their continuous input may lead to a high long-term concentration and promote continual, but unnoticed

effects on aquatic and terrestrial organisms. As such, it is important to screen and monitor these compounds in our waterways and to limit any possible sources of point pollution such as WWTPs and STPs. Monitoring these compounds is necessary to provide wider knowledge about their occurrence in the environment, to understand their fate, and organism exposure levels.

CONCLUSIONS

Oestrone (E1) and 17β oestradiol (E2) have been detected in Irish waters in both spot water samples and passive samplers. 17α ethynylestradiol (EE2) was detected in one passive sampler from Cork in 2013. While EE2 was not detected in spot water samples, the method LOD (limit of detection) does not meet the specified LOD for watch list; hence further development of such methods may potentially result in the detection of EE2 in some water bodies. Results from this study indicates that, for the coastal and freshwater sites studied, the presence of steroid oestrogens is low. Higher E1 and E2 levels were found in samples originating from higher population centres, e.g. Dublin and Cork, particularly at sites in close proximity to WWTP effluent discharges.

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. The results presented in this study are comparable to other European studies. One such example is a large-scale inter-laboratory comparison carried out in 2010 across 24 laboratories (Miege *et al.* 2012). This study included a number of polar pesticides from the WFD and compared different types of polar passive sampling, including POCIS. Similar $\mu g\,L^{-1}$ levels were detected and, as with this study, the passive sampling devices were found to allow determination of analytes that were otherwise rendered undetectable in the grab water samples. Similar recommendations were also made.

Overall, it is recognised that passive sampling undoubtedly provides a means by which low concentrations of hydrophobic pollutants (down to $pg\,L^{-1}$ 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 less biological influences such as size and metabolism; however, it is also clear that passive sampling still faces considerable challenges in order for its applicability to be demonstrated beyond doubt.

There is a role for passive sampling in both screening and trend monitoring and in feeding into risk-based approaches to operational monitoring with future derived passive sampling threshold values installed in an assessment hierarchy/framework where exceedance of the threshold value could be used to flag potential contamination issues.

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