URBAN WATER QUALITY MANAGEMENT

Passive Sampling a tool for Screening and Monitoring of New and Emerging Compounds

Fiona Regan[1], Lisa Jones[1] and Brendan McHugh[2]

[1]Dublin City University, Water Institute, [2]Marine Institute, Galway, Ireland

Abstract

The Irish Environmental Protection Agency, State of the Environment Report 2012[1] has identified the three main challenges for water quality management (i) to eliminate serious pollution associated with point sources (waste water treatment plants), (ii) to tackle diffuse pollution (pollution from agricultural activities and septic tanks), and (iii) to use the full range of legislative measures in an integrated way to achieve better water quality. The paper on the reform of the Water Sector in Ireland (DECLG, 2012)[2] confirmed the strategic importance of Ireland's water resources and signalled the Government's intent to take a national approach to water with the aim of conserving water resources and increasing the cost efficiency associated with water provision. From the State of the Environment Report the EPA has concluded that there is a pressing need to develop site-by-site actions for the water bodies reported as being at less than good status. By prioritising a subset of these each year, improvements can be made in rivers in the short term (with a slightly longer recovery time for lakes and estuaries). The challenge in relation to waste water treatment plants and associated water quality issues as well as diffuse pollution are dealt with in the case study presented. This project proposes a monitoring method (passive sampling) that can deal with challenges of chemical detection and occurrence in biota i.e. linking the occurrence in passive samplers to human health impacts. Arising from a catchment-based study over three-years using passive sampling for screening for emerging contaminants we propose that there is a role for passive sampling in feeding into risk based approaches to operational monitoring.

The policy challenge

The aquatic environment including lakes, rivers, ground water, estuaries and coastal zones, is vulnerable to changes induced by human activities. The EU Water Framework Directive (WFD) (2000/60/EC) aims to achieve and ensure good ecological and chemical water status and, moreover, to prevent deterioration of freshwater, transitional, coastal water bodies by 2015. Accurate classification of water body status with respect to WFD definitions and identifying trends poses a huge challenge in terms of monitoring activities. One major difficulty 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.

[1] EPA Irelands Environment An Assessment, Editors, Mícheál Lehane and Barbara O'Leary 2012.
[2] Reform of the Water Sector in Ireland, position paper DECLG, 2012.

A key challenge in proposing passive sampling as a monitoring technique for emerging contaminants in water lies in **meeting the requirements set out under the WFD and the Environmental Quality Standards** (**EQS) Directive**. 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 current recognized sampling method is grab sampling, which is both costly and time consuming and may still not be representative of actual conditions. Traditional biota monitoring is often hampered by the diversity of organisms employed (species selection), temporal variability, the collection of sufficient numbers of target organisms and physiological variability in response to environmental variables; thus complicating comparisons between regions, or against suitable assessment criteria or against EQS values.

Wider policy context

Good chemical status implies compliance with community Environmental Quality Standards (EQS) as defined by Annex IX and X of the WFD. Specifically, annex X of the WFD has identified a list of priority and priority hazardous substances with EQS for 33 substances set in WFD daughter directive 2008/105/EC. This list has recently been updated and expanded with a new daughter directive (Directive 2013/39/EU) to identify a number of emerging chemicals of concern, including pesticides and biocides, industrial chemicals and endocrine disruptors. Though, member states can monitor priority substances in water, biota or sediment, the EQS are primarily set for the water phase as annual average (AA) and maximum allowable concentrations (MAC) although biota EQS have been established for 11 substances. The directive also includes a new concept of a “watch list” of substances for which Union-wide monitoring data are to be gathered for the purpose of supporting future prioritisation exercises", and three pharmaceutical substances are identified for inclusion in the initial list. Although, in the marine environment the WFD only requires member states to achieve chemical status for territorial waters, the clear link to the WFD pollution methodologies for assessing chemical pollution are enshrined the Marine Strategy Framework Directive (MSFD Directive 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).

Intervention: Reasoning for reform and the introduction of the instrument

The changes to the current legislation on water quality, including the new watch list, in the EU have introduced a number of new priority substances to be monitored under the WFD as well as suggested ‘watch’ compounds. These new chemicals, termed emerging chemicals according to EU, include organohalogens, pharmaceutical compounds, endocrine disruptors and brominated flame-retardants. The EQS directive specifies that in order to monitor compliance of chemical parameters under the WFD, methods of analysis must be able to achieve limits of quantitation (LOQ) 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. Extraction of large 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 create practical difficulties for sampling (Loos 2012). From Table 1 it can be seen that while limits of detection for the emerging chemicals are allocated low values in water, in the cases where biota standards have been set these are often more achievable analytically, as is the case for hexabromocylcododecane (HBCDD) and dicofol. However, biota standards have not been provided for all priority and emerging substances, leaving water as the standard medium for analysis. Owing to the status of ‘emerging’ pollutants in many cases little work on the monitoring of the chemicals listed in Table 1 in water has been conducted.

Policy instrument design

It clear that the deployment of passive samplers to monitor the respective water bodies for longer periods of time, and providing time-weighted averages for priority substances would be a big step towards the level of monitoring required by the WFD. However, there are still some obstacles to be met before passive sampling is considered as 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 EQS set out in the WFD for the priority substances, with the exception of trace metals, are expressed as concentrations in 'total 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 level of suspended solids are low, it is often very difficult to reach the required limits of detection (LODs) by conventional means, and in this situation passive sampling could provide a useful alternative since they will take up the freely dissolved analytes in the water and have been shown to reach generally lower LODs than conventional grab samples (Vrana et al. 2005).

Table 1 Physico-chemical properties and environmental quality standards for emerging compounds recently included in the EU WFD (Directive 2013/39/EC). *Indicates 'watch-list' compound (COM(2011)876).

Substance	Use	CAS[4]	Log Kow	AA-EQS[4] Inland surface waters[5]	AA-EQS[4] Other surface waters	MAC-EQS[6] Inland surface waters[5]	MAC-EQS[6] Other surface waters	EQS Biota[3]
				µg L^{-1}				µg/kg wet weight
Dicofol	Organochlorine plant protection product	115-32-2	4.28	1.3 x 10^{-3}	3.2 x 10^{-5}	n/a[1]	n/a[1]	33
Perfluorooctane sulfonic acid and its derivatives (PFOS)	Industrial chemical with many uses	1763-23-1	N/A	6.5 x 10^{-4}	1.3 x 10^{-4}	36	7.2	9.1
Quinoxyfen	Fungicide	124495-18-7	4.66	0.15	0.015	2.7	0.54	n/a
Dioxins and dioxin-like compounds[1]	Combustion products and substances used in formerly used electrical equipment (PCBs)	[1]	6.8					Sum of PCDD +PCDF+PCB –DL 0,0065 µg.kg-1 TEQ (WHO 2005)[2]
Aclonifen	Herbicide	74070-46-5	4.37	0.12	0.012	0.12	0.012	n/a
Bifenox	Herbicide	42576-02-3	3.64	0.012	0.0012	0.04	0.004	n/a
Cybutryne	Biocide (antifoulant)	28159-98-0	2.8	0.0025	0.0025	0.016	0.016	n/a
Cypermethrin	**Insectidal pyrethroid**	**52315-07-8**	**6.6**	**8 x 10^{-5}**	**8 x 10^{-6}**	**6 x 10^{-4}**	**6 x 10^{-5}**	**n/a**
Dichlorvos	Organophosphorus insecticide and biocide	62-73-7	1.4	6 x 10^{-4}	6 x 10^{-5}	7 x 10^{-4}	7 x 10^{-5}	n/a
Hexabromocylcododecanes (HBCDD)	Flame retardant	[3]	5.07-5.47	0.0016	0.0008	0.5	0.05	167
Heptachlor and heptachlor epoxide	Organochlorine pesticide (legacy pollutant)	76-44-8/ 1024-57-3	5.44-6.10	2 x 10^{-7}	1 x 10^{-8}	3 x 10^{-4}	3 x 10^{-5}	6.7 x 10^{-3}
Terbutryn	Biocide	886-50-0		0.065	0.0065	0.34	0.034	n/a

17 α-ethinylestradiol*	Pharmaceutical: Synthetic steroid hormone	57-63-6	4.15	3.5 x 10^{-5}	7 x 10^{-6}	n/a	n/a	n/a
17β-estradiol*	Pharmaceutical: natural steroid hormone	50-28-2	3.94	4 x 10^{-4}	8 x 10^{-5}	n/a	n/a	n/a
Diclofenac*	Pharmaceutical: Non steroidal anti-inflamatory drug	15307-79-6	4.51	0.1	0.01	n/a[7]	n/a[7]	n/a

1 There is insufficient information available to set a MAC-EQS for these substances.
2 PCDD: polychlorinated dibenzo-p-dioxins; PCDF: polychlorinated dibenzofurans; PCB-DL: dioxin-like polychlorinated biphenyls; TEQ: toxic equivalents according to the World Health Organisation 2005 Toxic Equivalence Factors.'
3 Unless otherwise indicated, the biota EQS relate to fish. An alternative biota taxon, or another matrix, may be monitored instead, as long as the EQS applied provides an equivalent level of protection. For substances numbered 15 (Fluoranthene) and 28 (PAHs), the biota EQS refers to crustaceans and molluscs. For the purpose of assessing chemical status, monitoring of Fluoranthene and PAHs in fish is not appropriate. For substance number 37 (Dioxins and dioxin-like compounds), the biota EQS relates to fish, crustaceans and molluscs, in line with section 5.3 of the Annex to Commission Regulation (EU) No 1259/2011 of 2 December 2011 amending Regulation (EC) No 1881/2006 as regards maximum levels for dioxins, dioxin-like PCBs and non-dioxin-like PCBs in foodstuffs (OJ L 320, 3.12.2011, p. 18).
4 CAS: Chemical Abstracts Service.
5 Inland surface waters encompass rivers and lakes and related artificial or heavily modified water bodies.
6 This parameter is the EQS expressed as a maximum allowable concentration (MAC-EQS). Where the MAC-EQS are marked as "not applicable", the AA-EQS values are considered protective against short-term pollution peaks in continuous discharges since they are significantly lower than the values derived on the basis of acute toxicity.
7 There is not sufficient information available to set a MAC-EQS for these substances.

Project/Policy Outcomes

Passive sampling can be considered as a method of water monitoring under the WFD. In a study by (Stuer-Lauridsen 2005) it was found that passive samplers have the capacity to monitor over 75% of the organic micropollutants listed in water-quality criteria of the EU and US, the EU Water Framework Directive and the recommendations of The Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR).

Based on a three-year catchment study in Ireland using passive sampling study we propose that there is a role for passive sampling in both screening and trend monitoring in feeding into "tiered" risk based approaches to operational monitoring.

The recommendations arising from our project:

- While water, sediment and biota are the matrices of relevance for the WFD, with appropriate validation, for selected compounds PS show potential to provide at least as representative pollutant burden information as "conventional matrices".

- Working in tandem with EU guidance documentation there is a need amongst other research needs to close off biota/PS validation gaps, to work on statistical aspects to operational monitoring and to develop "common" monitoring tools for use at an 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.

- The potential for the inclusion of PS as standalone matrix for operational monitoring is high. The concurrent development of supporting EQScw 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) is now such that there is an on-going need to further enhance both national and international capacity building elements in the area of PS research and development.

- Strengths in numbers: Through focused integrated multi-state research and monitoring initiatives it may be possible to provide greater validation linking PS and biota, ultimately potentially leading to the development of widely accepted standalone EQScw suitable for supporting compliance goals.

- This project seeks to further discussion on a clear national strategy for the applicability of passive sample techniques (as part of a tiered approach) in water quality monitoring.