

Passive Sampling

Monitoring of the environment forms a key part of many regulatory activities. More traditional forms of sampling, whilst having a high degree of regulatory acceptance, have several flaws, so alternatives are being developed. A potential, 'new' complementary method is the use of passive sampling which involves the deployment of equipment for extended periods of time to continuously collect chemicals of interest prior to analysis. Passive sampling is advantageous over traditional 'grab' sampling methods as it can more readily provide data over temporal and spatial scales and could be of benefit in the environmental assessment of chlorinated chemicals.

What is passive sampling?

In many regulatory settings, environmental sampling plays a key role in characterizing (providing a baseline), monitoring (confirming the impact of any regulations) and investigating (determining the cause of any exceedances) the quality of the environment. Each specific 'role' though has a unique set of challenges associated with it, but all need a degree of certainty that the method used is capturing as much of the available information on environmental conditions, as reliably as possible.

Any certainty though is problematic as several factors (e.g. type of environment/ sample/ analytical method etc.) will determine which sampling mechanism is most appropriate. One of the 'simplest', and most widely used methods of sampling is the 'grab sample'. This is where a homogenous sample is collected all at once (e.g. filling a bottle with river water) prior to analysis. As a method, it already has a degree of regulatory recognition. However, the results do not tell you how conditions change temporally or spatially without significant investment in sampling frequency or infrastructure, and involves the collection of large volumes of water in order to detect trace chemicals. As such, complimentary methods are required.

The next 'level' of sampling is to conduct composite sampling where numerous individual, discrete (grab) samples are collected over time. This allows average conditions to be ascertained over the sampling period. However, this method suffers from its relative expense and from potential degradation issues when samples are not analysed immediately.

A solution to the above is to leave a material, *in-situ*, that continuously collects the chemical of interest from the environment into which it is placed. Passive sampling (PS) can enable the time-integrated measurement of contaminants in the environment with stability issues being avoided as the chemicals of interest are 'immobilised' onto the receiving material. This also allows an improvement in the detectable concentration limit (or LoQ). Whilst challenges remain with the potential for vandalism, fouling and the impact of variations in (e.g.) water flow, such devices are easy to deploy, require limited maintenance or external energy supply and can be deployed in a range of environments (e.g. remote sites with limited security or infrastructure). PS is particularly good for routine monitoring and allows low-cost, high-coverage sampling, indicating the 'average' levels of certain chemicals over time periods from several hours to several months.

Types of passive sampler?

PS has been known since the 1930s and has been employed in the sampling of air quality since the early 1970s. Since then it has found uses in the monitoring of work environments for occupational exposure monitoring. More recently this has extended to the study of chemicals in aqueous settings.

Two main types of sampler exist; those that contain materials into which target chemicals dissolve (**absorptive**) and those onto which chemicals 'bind' to the surface of the sampling material (**adsorptive**).

Absorptive (or partition samplers) work on the basis that, assuming there is sufficient time for the sampler to be exposed to the test chemical, an equilibrium is established. This equilibrium forms as the sampling material is chosen to have a higher affinity for the test chemical than the surrounding water, meaning it concentrates in the sampler, making it easier to measure. This feature means PS is particularly good for trace level and hydrophobic chemical monitoring. They tend to be made from materials like monophasic polymers (e.g. silicone rubber and LDPE).

Adsorptive (or polar) samplers bring about the strong binding of target chemicals to the surface of their sampling material, but do not necessarily rely on an equilibrium being formed. Examples include the Polar Organic Chemical Integrative Sampler (POCIS), Chemcatcher and Empore disk. Such samplers are better suited for hydrophilic chemicals including many substances of emerging concern.

How does it work?

In both cases, the sampling material can later be removed from the environment and the analyte extracted and analysed. The uptake of analytes in/onto the sampling material is controlled by the rate of diffusion, whose variables are well understood making it possible to calculate their environmental concentration. The uptake *process* is also well characterized as outlined in an excellent review by Deltares¹.

Given that any uptake by PS apparatus (and as a result the concentration that the sampler 'predicts' in the environment) can change due to a range of factors (such as temperature, initial concentration, presence of other contaminants, type of PS material), this innovative monitoring tool requires a degree of validation prior to its use in a

regulatory setting (such as calibration, handling, deployment, analysis and data interpretation).

Many studies on these validating factors have been published detailing the various deployment methods, analyte retrieval and calibration methods. From a regulatory perspective though, calibration is probably the most important of these and it can be performed in one of several ways:

- Static exposure - test sampler is exposed in a lab to a single volume of 'model' contaminated water and the depletion is assessed to predict sampler behavior in the environment;
- Static renewal - test sampler is exposed in a lab to batches of 'model' contaminated water with target chemical depletion then being assessed;
- Continuous flow - as the two above methods could eventually deplete the water without ever achieving equilibrium, this method aims to prevent the depletion of the chemical in the 'model' water phase by passing a constant supply of water through the exposure chamber of the test sampler and monitoring the presence of the target analyte in the effluent;
- In situ - this works 'in reverse' by measuring the dissipation rate of a reference analyte (a performance reference compound; PRC) that 'behaves' in a similar fashion to the target chemical. Due to the strong surface bonding associated with adsorptive PS (and limited release that therefore occurs), PRC usage is restricted to partition PS.

Solutions to common problems?

Another potential regulatory issue surrounds the potential fouling of PS equipment, particularly those deployed in aqueous environments. Here, aquatic organisms (such as algae) and debris may become entangled in the PS equipment and/ or biota colonize and begin to grow on the sampling material. This, along with variations in deployment temperature, has led to the development of an 'exposure adjustment factor' (or EAF) which is a ratio between the sampling rate obtained in the field and the rate obtained from compounds with similar physicochemical properties during laboratory calibration. This EAF can also be deduced from the loss of the (previously mentioned) PRC from partition samplers and is used to offset the effect of water flow rate, temperature and fouling on the sampler.

An aquatic passive sampler with both polar and partition sampling elements, prior to deployment.

Courtesy of F.Smedes, Deltares

Besides those scenarios listed above, PS also has the potential to be used as a *proxy* for sediment uptake to study contaminant partitioning. This would not only be of scientific interest but of benefit in industrial ‘duty of care’ scenarios; particularly given the cost of some remediation technologies. This requires some development.

Application to regulatory monitoring

PS can also help in various regulatory settings such as in the chemical mixture assessment under the Water Framework Directive (WFD) or the Marine Strategy Framework Directive. When used in combination with conventional grab sampling, PS can eliminate some of the pitfalls associated with the ‘spot sampling’ of priority substances. This is particularly useful in areas that are expected to show large temporal variation, mixing or fluctuation of contaminant sources.

Under the WFD (2000/60/EC), no monitoring tool is specified, but PS is identified as a potential *complementary* method that can be used to improve surface water assessment. The WFD identifies the need for the targeted analysis, in EU surface waters, of individual priority pollutants followed by the comparison of their concentration to a list of



environmental quality standards (EQS) to confirm surface water compliance. This list includes several chlorinated chemicals.

Complimenting WFD monitoring

As the chemical quality assessment under the WFD needs good tools, PS could be a cost effective approach to address the complexities of (e.g.) mix-

ture toxicity. At present PS cannot *fully* replace traditional methods though as it only assesses the dissolved phase (i.e. no WFD requested sediment ‘data’ are obtained).

One particularly complex mixture are those effluents from human activities. All surface waters can be potentially affected by such effluents; and a system of permits regulating the amount and type of discharge at a local level has therefore been developed in order to protect the environment. To date, impact assessments for specific effluent discharge permits have been based on general characteristics (such as volume, pH, temperature or biological oxygen demand), plus parameters such as levels of *specific* chemicals, with any requirements being based on industry activities.

Given the potential specificity, broad spectrum and time-integration of PS, it is a very useful tool in monitoring such effluents. However, as with many sampling regimes, PS must be used as part of a full evaluation (including ecotoxicology etc.) in order to conduct any ecological impact assessment to assess any mixture toxicity. As part of this process, care must be taken with PS such that:

- Certified reference materials/ inter-lab studies are applied to help validate sampling methods;
- Work to develop PS methods for highly ionic or hydrophilic substances is undertaken;
- Sampler investment/ operational costs, loss and vandalism are considered.

The future of passive sampling

Attempts are being made to compliment existing methods, in developing PS by applying biological analyses (bioassays) to directly evaluate potential toxicity. By coupling PS to ecotoxicological assessment, it may be possible to account for the complexities of mixtures; particularly as some partition samplers quite closely mimic the uptake processes of benthic organisms (e.g. mussels).

PS is a cost-effective sampling method that can capture a broad range of chemical compounds in the environment and ascribe a degree of temporal and spatial information to any results obtained. It compliments traditional methods in that, with development, PS can also be applied to various non-polar/ poorly water soluble chemicals, including several chlorinated substances.

As many of these molecules are investigated in regulatory monitoring frameworks, sometimes unnecessarily, Euro Chlor is following projects that addresses these exact PS development requirements.

1. <http://www.passivesampling.net/utrechtworkshop/pres/1202337-004-BGS-0027-r-The%20use%20of%20passive%20sampling%20in%20WFD%20monitoring.pdf>
(checked Feb 2016)
2. Miège *et al.* (2015). Trends in Environmental Analytical Chemistry 8, 20-26.

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Euro Chlor

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