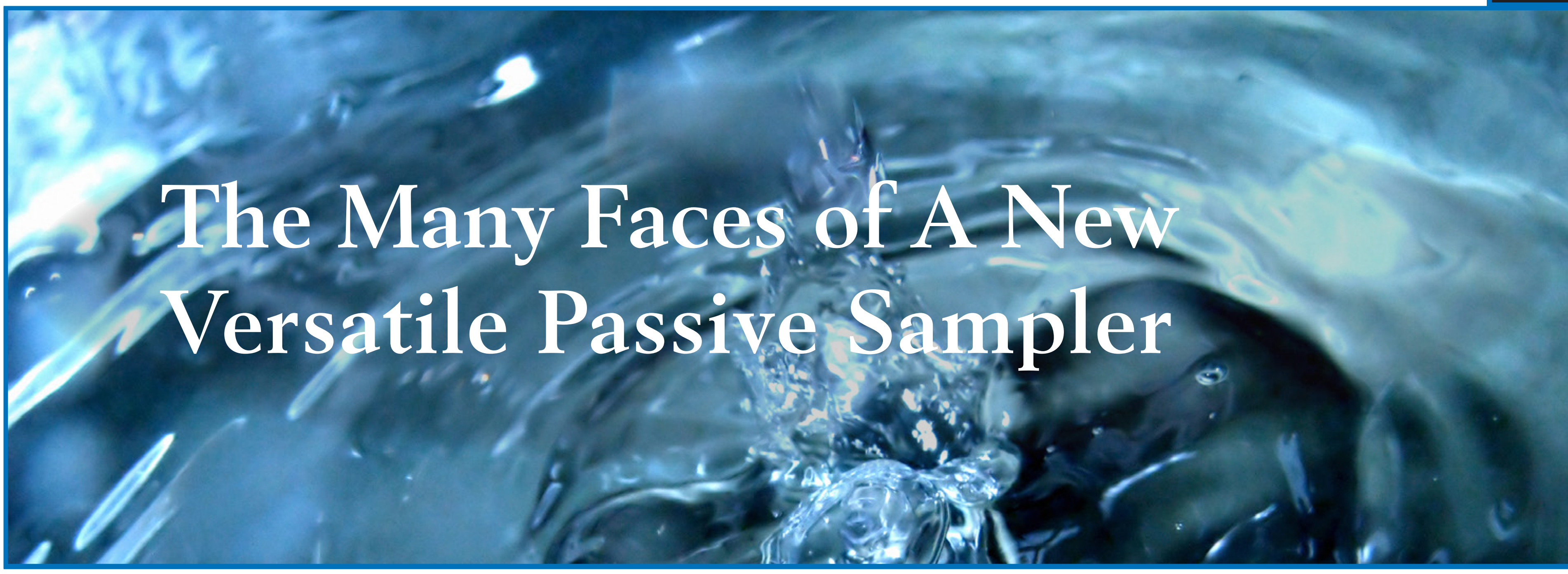

The Many Faces of A New Versatile Passive Sampler

Monitoring the concentration of chemicals in water is a statutory requirement across Europe (e.g. EU's Water Framework Directive [WFD]) and in most other countries. Most monitoring programmes involve the periodic collection of low volume spot (bottle or grab) samples of water that are analysed subsequently in the laboratory. Often the effectiveness of monitoring pollutants using this approach is challenging, particularly where levels fluctuate over time and when chemicals are present at trace, yet toxicologically significant concentrations. One solution to this problem is the use of passive sampling devices (PSDs). PSDs can be deployed in the environment for extended periods (from days to months) where they continually sequester compounds. For some analytes this can significantly lower their analytical limits of detection and enable the identification of pollutants that are episodically present.

> *"Chemcatcher® is now a highly versatile tool for screening and the quantitative/semi-quantitative assessment of different classes of chemicals in various aquatic environments. This device and other commercially available designs, offer potential for improving the quality of data in regulatory monitoring programmes."*

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PSDs are frequently used to obtain time-weighted average (TWA) concentrations of pollutants in the water column over a deployment period (Fig. 1). A similar approach is used for determining TWA concentrations of chemicals in the atmosphere. This type of information gives a more representative picture of the chemical quality of the environment over time. To obtain TWA concentrations samplers must first be calibrated in the laboratory to ascertain the uptake rate (measured as volume of water cleared per unit time i.e. L/day) for the pollutant of interest. For some samplers the uptake rate can be estimated from mathematical models using physico-chemicals properties of the compound under investigation. The period in which samplers remain in the time integrative mode is compound dependant and needs to be determined prior to deployment. Once this period is exceeded samplers eventually come to equilibrium with the ambient medium. An ISO standard (ISO 5667-23: 2011) concerning the use of passive samplers for the determination of priority pollutants in surface waters is available as a guide for end users.

A range of different PSDs is available both commercially and as research tools. Examples include the semi-permeable membrane device (SPMD), low-density polyethylene and silicone rubber membranes, diffusion gradients in thin films (DGT), polar organic compound integrative samplers (POCIS) and the Chemcatcher®. Here we describe how the Chemcatcher® is proving a robust and versatile monitoring device for measuring a number of different pollutants in the aquatic environment.

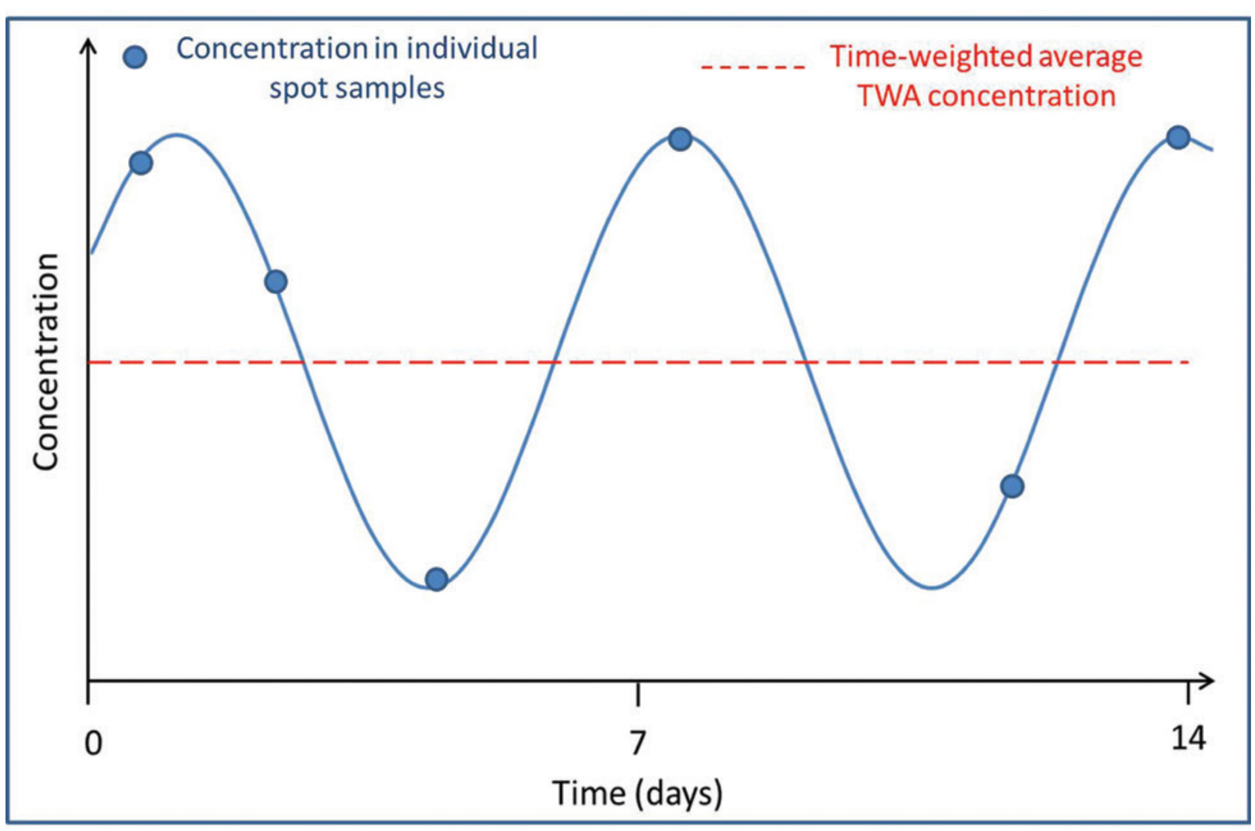

Fig.1. Variation in the concentration of a pollutant measured with six discrete spot samples over a 14-day interval versus the time-weighted average (TWA) concentration measured using a passive sampling device.

Chemcatcher®- a cost effective passive sampler

Chemcatcher® was developed at the University of Portsmouth, Portsmouth, UK. It comprises a low-cost, three component, watertight body manufactured from PTFE into which an appropriate 47 mm receiving phase disk is inserted (Fig. 2). Normally, this disk is covered with a thin 47 mm diffusion limiting membrane (e.g. low-density polyethylene, polyethersulphone or cellulose acetate) depending on the application. Various types of receiving phase can be used depending on the properties of pollutants being measured. Examples include 3M Empore™ disks (e.g. C8, C18, styrene-divinylbenzene (SDB), anion-exchange and chelating) and the Horizon Atlantic™ range of immobilised solid-phase extraction materials. The sampler sequesters the pollutants of interest and these are retained on the receiving phase disk. After retrieval pollutants are eluted from the disk using a solvent or acid and analysed using conventional instrumental methods (e.g. gas or liquid chromatography with mass spectrometry or by atomic absorption techniques). Samplers can be deployed in potable, surface, coastal and marine waters. Normally this design of sampler is not used for monitoring ground water.

Fig.2. Chemcatcher® passive sampler and a type of cage used for field deployments.

The many "faces" of the Chemcatcher®

The original design concept of the Chemcatcher® was to develop an easy to use sampler for monitoring a range of pollutant classes by altering the combination of receiving phase and diffusion limiting membrane used. The early applications were to measure TWA concentrations of non-polar organic compounds (e.g. PAHs, PCBs and specific pesticides) and heavy metals (e.g. cadmium, copper, lead, nickel and zinc). Subsequently, a number of new application areas have emerged (Fig. 3).

Fig. 3. Schematic of the different versions of Chemcatcher® for monitoring various types of environmental pollutants.

Non-polar organics Chemcatcher® - This sampler uses a C18 Empore™ disk overlaid with a thin low-density polyethylene membrane. In order to increase the uptake rate of analytes a small quantity of n-octanol is added between these layers during manufacture. Recent applications of the device include the measurement PCBs, PAHs and DDT (Petersen et al., 2015, Lobpreis et al., 2010). Using the same receiving phase with a cellulose acetate membrane the Chemcatcher® can measure organotin compounds including monobutyltin, dibutyltin, tributyltin (TBT) and triphenyltin (Aguilar-Martínez et al., 2008). The device was used to monitor TWA concentrations of TBT at marinas in Spain. High concentrations of TBT are often found at these locations as a legacy from the use of this compound as an anti-foulant in marine paints.

Polar organics Chemcatcher® - There has been recent interest in monitoring polar chemicals in water. This class includes 'emerging pollutants' such polar pesticides, pharmaceutical residues and associated metabolites and personal care products together their environmental degradation products. Several designs of Chemcatcher® are currently being used to sequester these types of chemicals. For example, Moschet et al. (2014) used a Empore™ SDB-RPS receiving phase in conjunction with a polyethersulphone membrane to effect an in-situ (samplers deployed directly in river water to measure uptake rates) calibration of the Chemcatcher® for 322 polar pollutants found in rivers impacted by agricultural run-off and urban inputs. For the majority of the substances there was a good correlation between those detected in water samples with those found on the receiving disks. This indicated that the Chemcatcher® was a suitable tool for the qualitative screening of polar chemicals in river water. South West Water Ltd. and the WestCountry Rivers Trust used a different variant (Empore™ anion exchange receiving phase and polyethersulphone membrane) of the calibrated device to investigate inputs acid herbicides (e.g. Mecorpop, MCPA, 2,4-dichlorophenoxyacetic acid) in the River Exe as part of the 'Upstream Thinking' initiative. The TWA concentrations were calculated and this allowed better estimates of the overall inputs of these herbicides into the catchment. In addition, the samplers detected sporadic inputs of these herbicides after rainfall events not picked up in spot water samples. A number of acidic pharmaceuticals (e.g. diclofenac, ibuprofen and naproxen) were also sequestered simultaneously on the anion exchange phase.

Metaldehyde Chemcatcher® - Metaldehyde is a molluscicide and is the active ingredient in formulated slug pellets. Large quantities of slug pellets are used in agricultural areas in the UK at specific times in the year to control infestations in crops. Metaldehyde is a polar chemical, being poorly retained in soil. Consequently, high concentrations can be found in surface waters after significant rainfall events. Often the concentrations of this pesticide exceed the legal Prescribed Concentration Value (PCV) of 0.1 µg/L. This becomes an issue when such surface waters are used for potable supplies; as metaldehyde is difficult to remove using conventional drinking water treatment processes. The University of Portsmouth working alongside South West Water Ltd. and Natural Resources Wales have developed a novel version of the Chemcatcher® for monitoring metaldehyde. The device is fitted with a Horizon Atlantic™ HLB phase receiving disk that has a high affinity for polar chemicals. Extensive field trials are now ongoing as part of a NERC funded 4-year industrial PhD CASE studentship involving these project partners.

Metals Chemcatcher® - Metals in water can be sequestered using a Chemcatcher® fitted with an Empore™ chelating disk. The performance of the device was investigated in relation to its application in regulatory (e.g. European Union's Water Framework Directive) monitoring of trace metals (e.g. Cd, Cu, Ni, Pb and Zn) in surface waters (Allan et al., 2007). These workers evaluated the responsiveness of the sampler to rapidly changing aqueous concentrations of metals and clearly demonstrated its ability to react to transient pollution events.

Nutrients Chemcatcher® - A recent addition to the family of devices is the development of a version for monitoring nutrients such as nitrate and phosphate (Knutsson et al., 2013). Here the sampler is fitted with an Empore™ anion-SR disk overlaid with a cellulose acetate membrane. The device was shown to selectively sample labile nitrate and phosphate species being confirmed by comparison of the analysis of spot samples using ion chromatography.

Radionuclides Chemcatcher® - The Fukushima nuclear reactor incident in 2011 led to the release of large quantities of radioactive isotopes into the environment. Of particular concern was the impact of radio-caesium in different environmental compartments. Fortuitously, 3M produced a special caesium RAD-disk as part of their Empore™ range. The University of Portsmouth team working with colleagues at the Chiba Institute of Technology, Tokyo and 3M Japan Ltd. investigated the use of this product as a receiving phase for the Chemcatcher®. It was found that this bespoke material had a high affinity for this element, enabled time integrative accumulations and lower analytical detection limits. It also negated the need to collect of large (c. 200 L) spot samples of potentially radioactive water. A number of monitoring campaigns using the Chemcatcher® by various agencies in Japan have been undertaken to investigate the environmental fate of radio-caesium and to assess the effectiveness of different remediation measures.

Conclusion

In recent years, there has been significant interest in the use of passive sampling devices either alongside or as a replacement to spot water sampling procedures. A number of devices is available for different types of pollutant and for varying field applications. In this article we have shown how the Chemcatcher® is now a highly versatile tool for screening and the semi-quantitative and quantitative assessment of different classes of chemicals in various aquatic environments. This device and other commercially available designs, offer potential for improving the quality of data in regulatory monitoring programmes.

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