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Advantages of passive sampling

With passive sampling, contamination of rivers can be analysed more comprehensively than with spot sampling. The method is suitable for capturing spatial and temporal patterns of pollutant inputs. It can also be used to detect substances present in waters at concentrations below the limit of quantification – for example, PCBs in the Birs river.



Chemicals in water diffuse into a passive sampler, accumulating in the silicone sheet.

Pollutants enter our surface waters by a wide variety of pathways. Many of these substances can now be reliably measured, and new methods allowing detection of additional substances are constantly being developed. All these analyses are de-

pendent on the collection of water samples, which frequently involves spot (or “grab”) sampling. But to what extent does analysis of individual spot samples provide an accurate and representative picture of the pollutant situation?

Inadequacy of spot sampling

Watercourses are highly dynamic systems. As a result of rain-fall, flow rates vary continuously, leading to differences in the dilution levels of pollutants. Inputs to surface waters are also dynamic, with run-off of pollutants from roads (often metals) or agricultural areas (often pesticides) occurring intermittently. Inputs from industrial processes also vary significantly over time. In addition, because it takes some time for substances entering a river or stream to be completely mixed with the water, they are not homogeneously distributed. All these factors make it very difficult to collect representative samples. In particular, if one wishes to find out whether water quality standards are being complied with or to determine where action is required, individual measurements are not sufficient for an assessment. Automatic samplers are only suitable for use at certain sites, such as outflow pipes or well-mixed river sections. Operation of such systems is also expensive and labour-intensive, which makes them less suitable for large-scale monitoring programmes.

An alternative is offered by passive sampling, where substances in water are retained by and accumulate in a sorbent material (see Box). This means that compounds can also be detected which are otherwise difficult to determine in a water sample because of low concentrations. Originally developed for the analysis of air pollutants, passive sampling has also been used over the last three decades to detect metals and hydrophobic organic pollutants in water [1, 2]. Methods for sampling hydrophilic organic substances in water were first introduced ten years ago. Researchers at Eawag and the Eawag/EPF Lausanne Ecotox Centre have been studying passive samplers for some time. Below, we discuss two examples illustrating the advantages of the method.

PCB source identified on the Birs

In 2008, the discovery of fish in the Birs river (Canton Jura) with concentrations of dioxin-like polychlorinated biphenyls (PCBs) far above the permissible limit was widely reported [3]. The cantonal authorities advised anglers to restrict their consumption of fish and even imposed a ban on fishing in certain particularly contaminated reaches. However, no indication of the possible source of PCB pollution was found in the fish. Therefore, at the suggestion of the Canton Jura environment agency and on behalf of the Federal Office for the Environment, a team of researchers from Eawag's Environmental Chemistry and Empa's Analytical Chemistry department collaborated with Cantons Bern, Basel-Landschaft and Jura to investigate whether passive sampling could facilitate the search for the source of the contaminant. This method appeared to us to be particularly suitable since passive samplers – like fish – continuously accumulate PCBs. Based on previous experience, we selected the polymer polydimethylsiloxane (silicone) as the sampling phase [2].

Silicone sheets were deployed at ten sites along a roughly 60-kilometre stretch of the Birs. After an exposure period of several weeks, we extracted PCBs from the samplers and established the contamination of the river. Thanks to these analyses, it was possible to pinpoint the source of the inputs (Fig. 1). A second measurement campaign subsequently identified an industrial site as the source of contamination. Remediation measures were then rapidly initiated by Canton Jura so as to prevent further inputs of PCBs. Initial follow-up controls indicate that the measures have been worthwhile, as contamination has decreased sharply. Following the success of this study, silicone passive samplers have also been used for PCB monitoring in the Saane and Aare rivers and in the Rhône catchment.

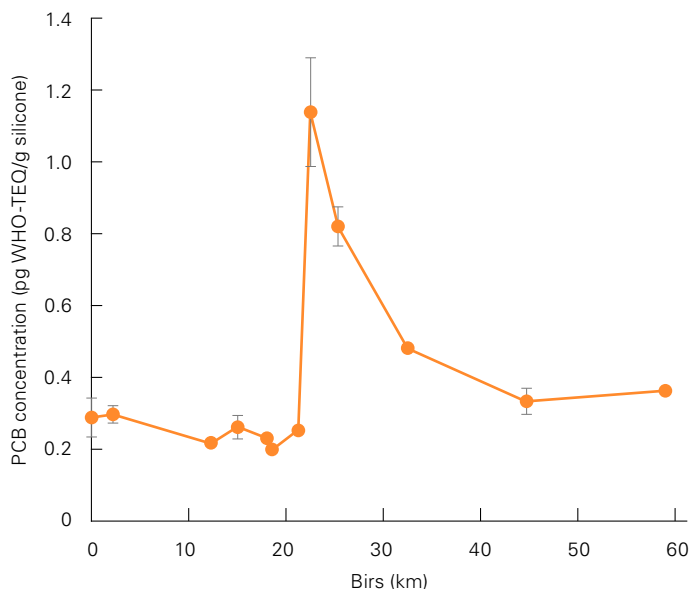


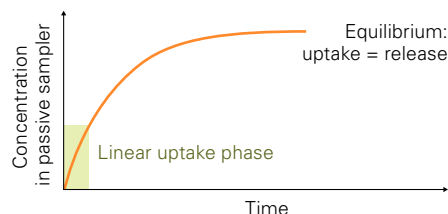
Fig. 1: PCB concentrations (expressed as toxic equivalents) measured along the Birs river. The input source is clearly identifiable.

Passive samplers

In passive sampling, substances diffuse from the sampled medium (e.g. water, known as the donor phase) into the receiving phase of the device. The process is driven by a difference in the chemical activity of substances in the two phases. Compounds are retained on the surface of the sampler, where further diffusion and sorption processes occur. Depending on the target compound, lipids, solvents or polymers may be used as the receiving phase.

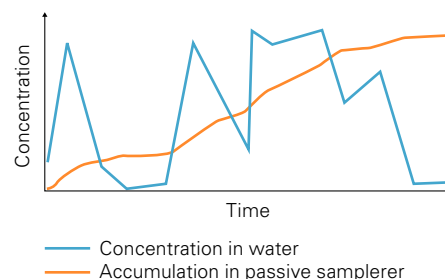
Substance flow from the water phase to the receiving phase is proportional to the difference between the chemical activities in the two phases. If this difference is large enough, a compound will accumulate continuously in the sampler. Initially, accumulation proceeds at a constant rate and the curve is practically linear. For accurate sampling, it is important that the exposure duration should fall within this phase, well before a state of equilibrium is reached (see top figure). Fluctuating concentrations in the water lead to differences in the amounts of a substance that accumulate at different time points. In this way, variable concentrations can be integrated over a given period (see middle figure).

Passive samplers widely used for analysis of organic pollutants are Chemcatcher and POCIS (polar organic chemical integrative sampler). In these devices, a solid receiving phase is covered by a membrane (see photos on the right). The samplers are mounted in holders for deployment in rivers. After an exposure period of several weeks, the devices are retrieved and substances are extracted from the receiving phase and analysed.



As the rate of accumulation of a substance in a passive sampler is constant in the linear phase under stable environmental conditions, the increase in the amount of substance in the sampler is proportional to the concentration of the substance in the water.

Substance uptake at a constant concentration in water. The concentration in the sampler increases until equilibrium is reached between uptake and release.



Various types of passive samplers. a) Silicone sheets for sampling of polychlorinated biphenyls, b) POCIS device, c) Chemcatcher for sampling of hydrophilic organic contaminants.



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Passive sampling combined with bioassays

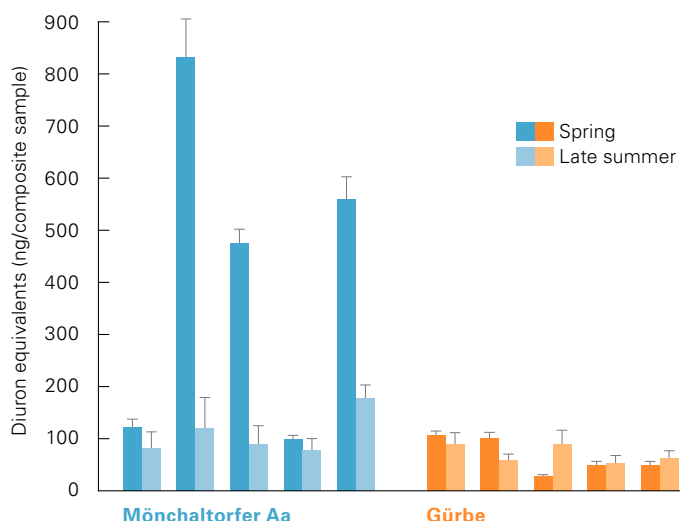
Passive sampling was also employed in the “Integrated River Water Quality Management” project, a collaborative effort involving several Eawag research departments (www.eawag.ch/iwqa). The project – part of the National Research Programme “Sustainable Water Management” (NRP61) – aims to characterize in detail the state of the Mönchaltorfer Aa and Gürbe river catchments. Decision-making support is to be developed to permit the assessment and minimization of adverse effects on the ecological state of watercourses. The influence of various management measures over the long term is to be assessed with the aid of a mathematical model. On both rivers, passive samplers were deployed in order to obtain more representative average pollutant values than would have been possible with low-frequency spot sampling. In addition, after prolonged exposure, the samples collected were sufficiently large to al-

low water quality to be assessed by means of various chemical analyses and bioassays.

Samples were collected from both rivers over a two-week period using Chemcatcher devices (see Box). The sampling phase used was a granulated sorbent fixed in a polytetrafluoroethylene (Teflon) matrix. Water quality was then assessed at the Ecotox Centre with the aid of three different bioassays. An algal assay was used to analyse samples for herbicides that inhibit photosynthesis. Using an enzyme inhibition assay, it was possible to detect insecticides that disrupt signal transmission in nerve cells. Lastly, genetically modified yeast cells were used to screen for substances with estrogenic activity.

As is shown by the algal assay, for example, passively collected samples provide a detailed picture of river water quality. Firstly,

Fig. 2: Herbicide concentrations observed at five sampling sites in the Mönchaltorfer Aa and Gürbe rivers. The values given are averages calculated for six passive samplers (composite samples), expressed as “diuron equivalents”. The diuron equivalent concentration is the concentration of the herbicide diuron that produces the same biological effects in an algal assay as the herbicide mixture present in the sample.



they effectively revealed spatial variation of pollutant concentrations in the Mönchaltorfer Aa and Gürbe catchments. Thus, herbicide concentrations were found to be markedly higher in various sections of the former river than in the latter. At the same time, passive sampling also revealed temporal variability: for both rivers, samples collected in May showed higher herbicide concentrations than in the late summer (Fig. 2). This reflects the increased application of crop protection products at the start of the growing season. In a previous study, we had already demonstrated that passive sampling is an effective method for the determination of pesticide concentrations in treated sewage effluents [4].

Taking environmental factors into account

Although passive sampling – in combination with chemical analysis or bioassays – has already produced useful results, there is still room for optimization. For example, not all substances accumulate in a sampling phase at the same rate. Compared to mixtures of substances that accumulate slowly, the toxicity of rapidly accumulating mixtures will tend to be underestimated in passive sampler extracts, even if both mixtures would be equally toxic to aquatic organisms.

The diffusion processes which determine the uptake of chemicals depend on environmental factors, such as temperature or flow conditions, and on the dimensions and design of the sampler. The question of how flow rates and diffusion-limiting membranes affect uptake in passive samplers has been studied by the Environmental Chemistry and Environmental Toxicology departments of Eawag. For this purpose, we set up a modular

channel system for river or wastewater, which can be spiked with chemicals (Fig. 3). It was shown that in passive samplers without membranes (e.g. silicone sheets or Chemcatcher devices with naked disks) the rate of accumulation is higher at a higher flow rate. This is because, with increasing flow rates, diffusion paths become shorter as a result of hydrodynamic effects. Such findings can be used to normalize field data and improve assessments.

Difficulties in determining concentrations

If passive sampling data (amount of substance per sampler per unit time) are to be used to determine substance concentrations in water, the samplers need to be calibrated. Calibration may be carried out in the laboratory. This process involves exposing passive samplers for different periods to water spiked with chemicals and determining uptake kinetics on the basis of the amounts accumulated. Alternatively, field calibration is also possible. Here, samples are collected at regular intervals in an initial measurement campaign. The sampling rate can then be calculated from the average substance concentration in the water, the amount taken up by the sampler and the exposure period. For example, if the average concentration is 5 nanograms per litre and 50 nanograms is taken up over a 10-day period, then the sampling rate is 1 litre per day. In subsequent measurements, the amount of substance accumulated is divided by the sampling rate and exposure time to obtain the estimated substance concentration in the sampled water [5].

This approach works well if conditions in the field are similar to those under which calibration is performed. But in reality,

Fig. 3: In a modular flow channel experiment, Junho Jeon and Etienne Vermeirssen investigate how the sampling rate in passive samplers is affected by the membrane and environmental conditions [6].



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environmental conditions, such as flow rates, vary continuously. So, even if sampling rates are known, the determination of substance concentrations by means of passive sampling also involves uncertainties. When bioassays are used, it is often not possible to estimate concentrations, as in such cases the samples analysed are usually mixtures. If it is not known what substances are present in the mixture, sampling rates cannot be determined and the toxicity of a sample can only be expressed in terms of amount per sampler rather than per litre of water.

Need for optimization and standardization

To improve the reliability of information on substance concentrations provided by passive sampling, further research is required [5]. But despite the limitations in this area, the method is already suitable for obtaining spatially resolved data on pollutant concentrations in rivers and identifying sources of contamination. In addition, temporal patterns of inputs can be reliably determined and followed over extended periods. Passive sampling delivers considerably more meaningful results than individual grab samples and is inexpensive and not unduly labour-intensive.

Another advantage lies in the fact that, over time, larger quantities of substances accumulate in passive samplers. Accordingly, it may be possible to detect substances – as in the case of PCBs in the Birs – because concentrations in the sampler are above the limit of quantification, or – as in the project on the Mönchaltorfer Aa and Gürbe rivers – to analyse samples using several different methods. Within the international NORMAN network of reference laboratories, to which Eawag and the Eco-tox Centre belong, efforts including large-scale interlaboratory tests are currently under way to further optimize and standardize passive sampling.

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