

Passive sampling for monitoring fate and transport of organic contaminants – field examples

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Abstract

Passive samplers provide a simple and robust monitoring tool used in order to monitor the transport and fate of organic and inorganic pollutants in the water phase. Current legislation stipulates that pollutants must be quantified, often at very low concentrations and under challenging conditions. Passive samplers are able to satisfy these needs. Through research and consultancy projects, the Norwegian Geotechnical Institute is working towards the wider employment of passive samplers to monitor a diverse range of contaminants. The case studies presented illustrate the ways in which passive samplers can be used in order to determine the freely dissolved pollutant concentrations and use these data in order to select site remediation, monitor concentrations over time, investigate the life cycle of pollutants in waste and assess water quality. Such a method can be widely applied within the realm of risk assessment and compliance.

Background information

Passive sampling

The introduction of pollutants in to the environment around us is a constant threat. Often the concentrations of such pollutants are very low and their detection is challenging. One method

that provides a solution is the use of passive samplers. The principle of passive sampling is based on the free flow of pollutant molecules from the sampled medium to a sampling device as a result of a difference in pollutant chemical potential in the two media as shown in figure 1. This means that when the sampler is placed in water, sediment or soil, pollutants are taken up and aqueous concentrations (if the media is water), or pore water concentrations (if the media is soil or sediment) can be deduced down to very low trace concentrations (1 part per quadrillion can be achieved). This established sampling tool is scientifically accepted and widely applied (Jonker and Koelmans, 2001, Hale et al., 2010, Lohmann 2013).

Passive samplers measure only the freely dissolved water concentration as they do not sample pollutants sorbed to colloidal matter. Passive samplers are easy to use, low cost, have minimal handling and analytical needs, can detect and concentrate very low freely dissolved pollutant concentrations and do not deplete or metabolise accumulated compounds (Lohmann 2013).

The passive sampling niche

Environmental compliance with existing and new legislation is necessary in order to maintain and improve the quality of the environment. With an ever increasing number of pollutants requiring monitoring, and more stringent

environmental quality standards being put in to place, there is a need for a low cost yet reliable method for measuring contaminants at trace levels. In addition to traditional legacy contaminants, emerging contaminants including pharmaceuticals, brominated flame retardants and re-emerging contaminants such as mercury can be monitored using passive sampling methods.

Regulators and companies are realising that passive sampling is a superior way of collecting data for risk assessment, coastal monitoring programs and even discharge permit reporting. Traditional monitoring methods fail to capture the very low trace concentrations that passive samplers have the ability to detect. There is also an increasing demand from companies and regulators to track contaminant transport, as well as to locate and quantify active emission sources. Passive sampling provides a unique way to do this.

Passive samplers compared to whole water sampling

The deployment of passive samplers in contaminated water provides an advantageous method

for determining water concentrations as compared to traditional water sampling. This is illustrated in figure 1 below using an example of a monitoring campaign from the United Nations Environmental Program. In order to detect concentrations of 0.001 pg/L PCBs both total water sampling or the deployment of passive samplers could be used. Using total water sampling, 10,000 L of water must be sampled and extracted with solvent in order to be able to detect such a low concentration of PCBs. However, the same concentration can be monitored by using just 10 g of a passive sampler. This provides a simpler, easier and less costly method for environmental monitoring. In addition the concentration of pollutants sampled by a passive sampler gives a time weighted average concentration, thus the concentration is not heavily influenced by for example a sudden point source input. Taking a single water sample, or grab sample as it is called, gives a single snap shot in time concentration.

Freely dissolved concentrations

By using passive samplers to measure freely dissolved concentrations a much better assessment

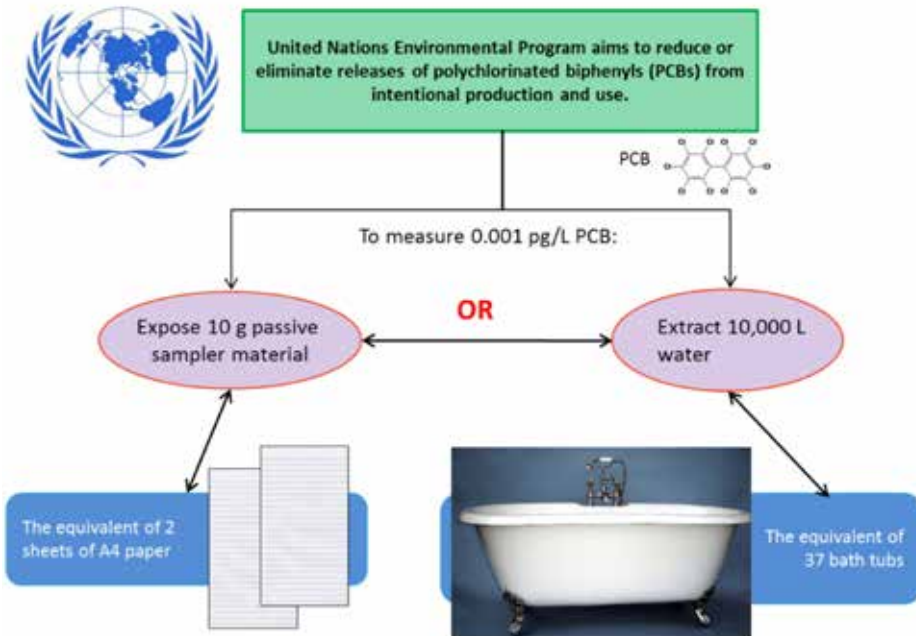


Figure 1. The advantage of deploying passive samplers in water compared to whole water sampling.

of risk can be obtained. The freely dissolved sediment pore water concentration has been shown to be a better proxy for the level of contaminants able to adversely affect biota and leach to surrounding soil and sediments (Kraaij et al., 2003; Vinturella et al., 2004; Ehlers and Loibner, 2006; Hawthorne et al., 2007a; Friedman et al., 2009), compared to total soil or sediment concentrations (Cornelissen et al., 2006b). These findings lend further support to the notion that the freely dissolved pollutant fraction should be quantified to determine soil/sediment risk. By determining the exposure of soil and sediment pollutants and measuring their effects on biota, trigger values based on total concentration of pollutants could be adapted to include an evaluation of bioavailability. For example, a comparison of freely dissolved contaminant concentrations could be made with environmental quality standards, such as those defined in the Water Framework Directive (Directive 2000/60/EC), after pollutant sorption to dissolved organic matter and suspended particulate matter has been accounted for.

The use of passive samplers in the field

Passive samplers have a very important role to play in the monitoring of the fate and transport of pollutants in the real world. This is an important niche that the Norwegian Geotechnical Institute is focusing on. Some key applications are illustrated below through the use of real field examples that are grouped according to:

- Pollutant source identification
- Tracking the fate and transport of pollutants in water (ground, surface and fjord), sediment and air
- Pollutant monitoring in combination with complimentary methods
- Risk assessment

Pollutant source identification and monitoring

Within the research project **WASTEFFECT** funded by the Norwegian research council (www.ngi.no/wasteffect) a robust waste emission and exposure model for waste regulators and compa-

nies to anticipate and reduce risks from emerging contaminants is being developed. The first phase of the project is the development of an emissions inventory of contaminants from various waste fractions, treatment methods and inventory compartments. Such information provides knowledge about the fate and transport of pollutants during and after waste handling processes. Brominated flame retardants (BFRs), bisphenol A the endocrine disrupting compound, and antimony (Sb), a toxic metalloid are being focused on.

Passive sampling strategies have been developed in order to determine the concentration of these pollutants in various waste streams. Diffusive Gradients in Thin-films (DGT) devices have been used in order to measure the freely dissolved concentration of Sb. DGT devices utilize a ferrihydrite gel layer ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$) to control the diffusive transport of metals in solution to a cation-exchange resin. The resin used in DGT (Chelex) is selective for free or weakly complexed species and therefore provides a proxy for the freely dissolved concentrations of metals in solution. BFRs and BPA have been measured in the water phase and in the air phase with the use of several different types of passive sampler membrane materials. Freely dissolved concentrations of BFRs and BPA have been determined with the use of polydimethylsiloxane and polyoxymethylene (POM) respectively, and air concentrations of contaminants have been sampled with the use of XAD beads, a type of polystyrene copolymer resin. Figure 2 provides photographs of the passive samplers that have been used.

Tracking the fate and transport of pollutants in water, sediment and air

The Impact of Climate Change on the Quality of Urban and Coastal Waters - Diffuse Pollution (diPol) project aimed to identify impacts and suggest measures to reduce adverse consequences of climatic changes impacting the quality of urban and coastal waters. The project was supported via the EU Interreg IVB North Sea Region programme (<http://www.tuhh.de/iue/dipol/homecopy-1.html>). Several countries participated in



Figure 2. The passive sampling devices used in the WASTEFFECT project. From left to right; DGT used to sample Sb, polydimethylsiloxane and polyoxymethylene used to sample BFRs and BPA, respectively, in water (both membrane materials are encapsulated in a stainless steel cage) and XAD beads (contained in the tube which is protected by the stainless steel cage).

the project, with each partner choosing a water body to investigate, and measuring, among other factors, the concentration of organic pollutants. The inner Oslo fjord was chosen as the Norwegian water body and the total water concentration of PAHs and PCBs as well as the freely dissolved concentrations were measured using total water sampling (taking a grab water sample



Figure 3. The polyoxymethylene passive sampling device used to measure PAHs and PCBs in the inner Oslo fjord.

and extracting it with solvent) and with polyoxymethylene passive samplers as shown in figure 3. The samplers were immersed in the water at four different locations for up to two months at a time, three times a year and for two years. Complimentary data was obtained by taking total water samples and determining the freely dissolved concentrations as waste input streams could be inferred. By following concentrations over time, temporal and spatial patterns could be identified.

During a Norwegian Research Council funded project under the Havkyst program: *Old sins or ongoing input? Passive samplers as a novel tool for flux determination in sediment-water-air systems*, research was carried out again in the Oslo fjord in order to compare the environmental burden of continual pollutant inputs and contamination remaining from “old sins”. Passive samplers were used in a very novel way throughout the research as they were deployed in the air, the water and the sediment phase. Photographs of the devices used to sample the air and water phases are shown in figure 4. Using the passive samplers in such a way allowed the movement of the pollutants between environmental compartments to be tracked, a vital piece of knowledge when considering the fate and transport of pollutants on a large scale.

The results obtained revealed that there is a continual input of phenanthrene from the air



Figure 4. Photographs of the polyoxymethylene passive sampler devices used to measure the air and water PAH and PCB concentrations, respectively.

phase to the water phase. In addition, for both PAHs and PCBs, the sediment was shown to be the environmental compartment that is the main source of contamination to the overlying water. Therefore, “old sins” are still impacting the water in the Oslo fjord to this day. A summary of the results is given in figure 5.

A *landfill* used between 1953 and 1965 for industrial waste from a Hydro power plant containing PAHs, heavy metals, oil and tar provided a field case study for the comparison of passive sampling methods and total water sampling. Passive samplers made of polyoxymethylene to sample organic compounds and DGT devices to

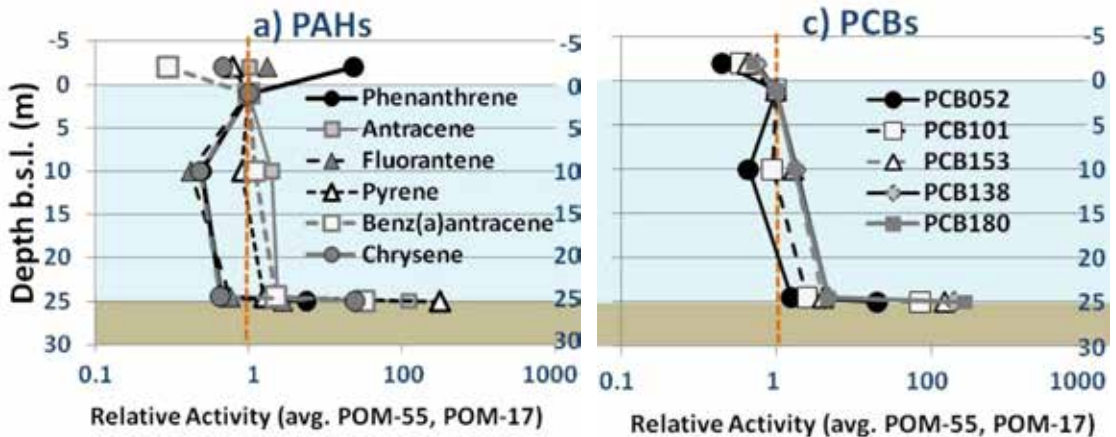


Figure 5. Overall results from the project X. Relative activity is indicative of whether the environmental compartment is a source (value over 1) or a sink (value under 1) of pollution.



Figure 6. the passive sampling device. The red buoy was used in order to mark the device. One either side of the buoy is the POM passive sampler and the DGT.

sample metals were placed upstream, just outside and downstream the landfill in order to track changes in concentration spatially. Figure 6 illustrates the device that was deployed.

Total water concentrations were measured by taking water samples from ground water wells. Interestingly, the concentrations measured in the ground water well samples were higher than those measured using passive samplers. All of the passive samplers displayed similar concentrations showing no evidence of increasing concentrations just outside the landfill compared to upstream the site. Although the total water concentrations were higher than the freely dissolved concentrations, the passive sampler results allowed the conclusion to be drawn that pollutants were not being released from the landfill in its current state. This therefore illustrates that the risk of pollutant spreading from groundwater to the water body is small. By just measuring concentrations in the ground water wells, such a conclusion would not have been reached.

Pollutant monitoring in combination with complimentary methods

Passive samplers can also be combined with biological sampling in order to provide complimentary data for a monitoring campaign. Such an approach was taken at a *site where a spill of PCB containing oil in to the sea* occurred. Following the implementation of measures to ensure that the further leaching and environmental deterioration would not occur, a monitoring program

based on the use of mussels and polyoxymethylene passive samplers was carried out. Approximately 20-50 mussels were collected from 5 monitoring stations, shown in figure 7 below, and passive samplers were deployed for between one and three months.

Both the passive samplers and the mussels showed that concentrations of PCBs decreased with increasing distance from the site of the spill. Both monitoring tools showed that the measures implemented to prevent further leaching had been successful.

Risk Assessment

The use of passive samplers within the realm of contaminated soil and sediment risk assessment has gained more and more attention recently. Passive samplers can also be used in order to determine how strongly pollutants are bound to contaminated soil or sediment, which is a pivotal piece of information when the risk such pollutants pose via leaching and spreading to the surrounding environment needs to be considered. By carrying out a simple laboratory experiment in which passive samplers are exposed to the contaminated soil or sediment, the soil or sediment – water partitioning coefficient value (K_d) can be determined. Indeed, in the model developed by Miljødirektoratet to assess contaminant spreading and the negative effect it could have on the environment, the use of site specific input model parameters are encouraged. In this context, the determination of the soil or sediment-water partitioning coefficient for a particular pollutant can be used and reduce the inherent conservatism in the model.

This input parameter was determined for contaminated soil samples taken along the pipe line of *a hydro power plant*. A series of sand blasting activities, inside and outside the pipe line that leads water down to the power plant at the bottom of the hill, has resulted in the contamination of the surrounding soil with PAHs from the coating of the pipes, as shown in figure 8. A thorough risk assessment was undertaken in order to assess the most important spreading and transport routes for the PAHs in order to

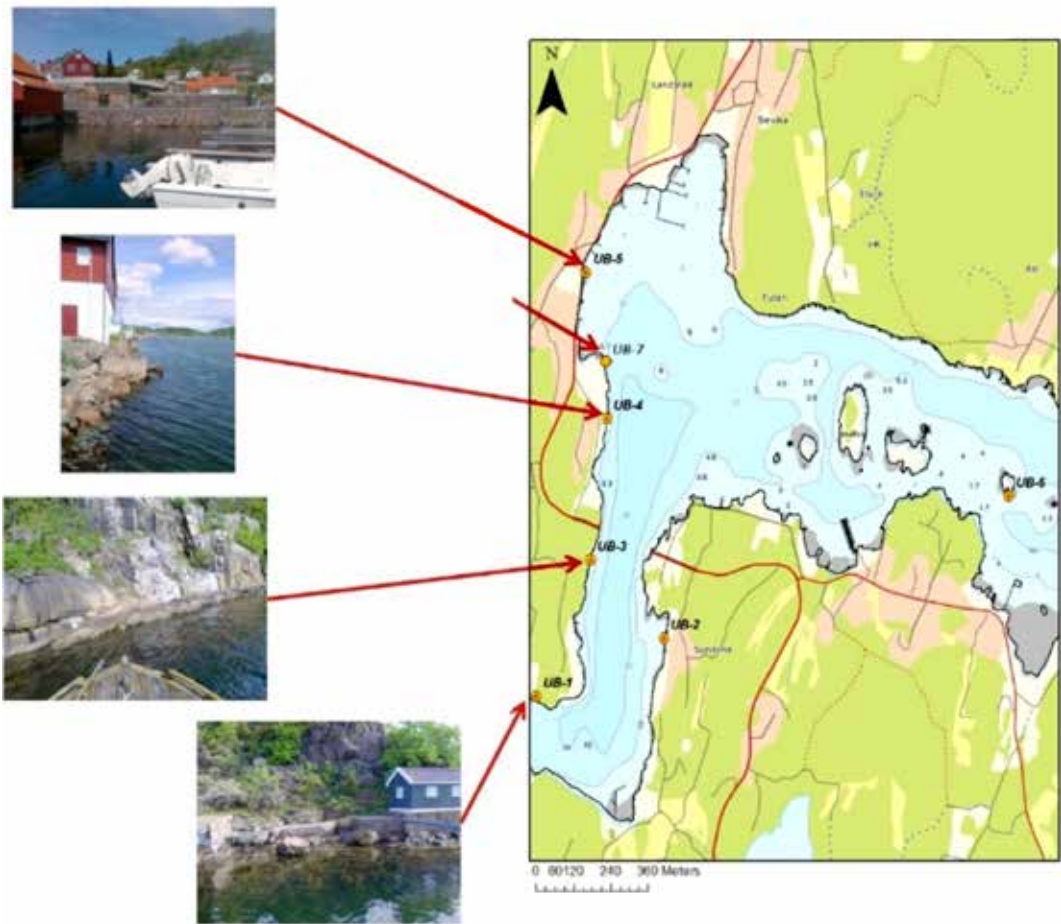


Figure 7. The monitoring stations from which mussels were collected and passive samplers were deployed.



Figure 8. The hydro power plant and the pipeline from the top of the hill leading down to the power plant.

suggest the most appropriate remediation method. Through the use of Miljødirektoratets guidelines (Veiledning om risikovurdering av forurenset grunn og sediment) and their work tools, a three step risk assessment of the site was carried out.

Passive samplers were used to measure site specific leaching of PAHs from the contaminated soil and the resulting soil-water partitioning coefficients were used as input parameters for the work tool in the risk assessment. The site specific soil-water partitioning coefficients were determined to be 250 to 4800 times higher than those used in the model as default parameters. This means that PAHs in this particular soil were much more strongly bound to the soil than the risk assessment model assumed. The PAHs are therefore much less available to organisms and to leach to the surrounding soil, than estimated from the standard values. This knowledge proved especially useful in the selection of the most suitable remediation strategy.

Outlook

All of the case studies above illustrate the vital role passive samplers can play in monitoring the fate and transport of pollutants in the water environment. The ease of use and reproducibility of results that passive samplers provide ensures that they will become a standard and relied upon monitoring method of the future. Instead of single point observations they help us to get an impression of a time averaged exposure of the environment which will be critical for understanding the real risks for human health and the environment.

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