Combining biota and passive sampling for contaminant monitoring

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Summary

This paper is based on a presentation given at the Norwegian Water Association meeting of the 23rd September 2013. We have supplemented this with a discussion of the use of passive sampling for regulatory monitoring (based on a NORMAN Expert Group meeting "Linking Environmental Quality Standards and Passive Sampling" held in Brno, Czech republic on the 3rd and 4th July 2013).

Sammendrag

Denne artikkelen er basert på en presentasjon gitt i et møte i Vannforeningen 23. september 2013. Artikkelen er supplert med en diskusjon om bruk av passiv prøvetaking til lovpålagt overvåking (basert på et NORMAN ekspert gruppe møte med tema "Linking Environmental Quality Standards and Passive Sampling" avholdt i Brno, Tsjekkia 3. og 4. juli 2013).

About passive sampling technique

The passive sampling technique is based on the diffusive transport of substances from the environmental medium being sampled into a precleaned polymeric device in which they accumulate because of absorption or adsorption processes. For passive sampling of hydrophobic contaminants the most known sampler is the SemiPermeable Membrane Device (SPMD), a low density polyethylene membrane containing a triolein lipid phase, intended in the first instance to simulate passive hydrophobic contaminant uptake by organisms (Huckins et al., 2006). Presently, single phase samplers constructed from polymeric material such as low density polyethylene or silicone are applied as they are more robust and exhibit a simpler uptake model (Allan et al., 2009; Allan et al., 2010). At equilibrium, the mass of a chemical measured in the sampling device can be related to the freely dissolved concentration of contaminants in water it was exposed to through the sampler-water partition coefficient ($K_{s\text{-}w}$). Passive sampling methods enabling to derive freely dissolved contaminant concentrations have been the subject of significant developments over the last 20 years (Vrana et al., 2005). For highly hydrophobic contaminants, polymeric samplers have a large capacity and often will not attain equilibrium during typical deployment period of a few weeks. Uptake in the linear regime (i.e. far from equilibrium) allows to obtain a time-integrated concentration for the deployment period in water. This time-integrated freely dissolved concentration can be calculated with knowledge of in situ sampling rates, R_s, equivalent

Figure 1. Passive sampler deployment in water.

amount of water sampled per unit of time (L d^{-1}). Freely dissolved concentrations derived from passive sampling have shown excellent relationship with concentrations accumulated in parallel deployed mussels (Smedes, 2007).

These passive sampling techniques have been applied in- and ex- situ to obtain a measure of freely dissolved/available concentrations in various other abiotic environmental compartments such as wastewater, air and sediments. Evidently, in the case different environmental compartments in contact with each other (e.g. water, sediment, air or organisms) are at equilibrium, passive samplers deployed in each of the individual compartments will lead to identical measurements. In contrary, differences in passive sampler measurements in various compartments would indicate disequilibrium. This view led more recently to the development of *in tissue* passive sampling (in vitro) where samplers were deployed in intact fish tissue (Jahnke et al., 2011).

Earlier work based on immersing silicone material in various lipids to estimate lipid-silicone partition coefficients, $K_{lip\text{-}s}$ (Jahnke et al., 2008) showed similar partitioning properties for lipids representative of organisms at different trophic levels. For hydrophobic non-ionised persistent organic pollutants such as chlorinated (e.g. hexachlorobenzene or polychlorinated biphenyls, PCBs) and brominated (polybrominated diphenylethers, PBDEs) concentrations in biota are most often expressed on lipid basis as lipids are generally assumed to be the main component responsible for the accumulation of these contaminants in biota. Such lipid-based biota concentrations agreed very well with concentrations by in vitro fish tissue-exposed silicone assays converted to a lipid basis using the $K_{lip\text{-}s}$ (Jahnke et al., 2011).

In vivo implantation passive sampling

This year, we reported the use of in vivo implantation passive sampling for an equilibrium measurement of hydrophobic contaminants in caged brown trout (*Salmo trutta*) exposed in the Alna River in Oslo (Allan et al., 2013a). In this study, PCB concentrations measured in silicone tags inserted in the fish cavity for 28 days that when converted to lipid basis were in agreement with directly measured lipid based concentrations in the fish. Silicone samplers (Allan et al., 2010; Allan et al., 2013b) were deployed alongside the caged fish. Ratios in (equilibrium) concentrations of fish- and water-exposed samplers close to one indicate apparent equilibrium between the fish and the water (e.g. for some of the PCBs) while ratios well below one such as those found for pyrene and fluoranthene are indicative of metabolism in the fish. This in vivo implantation methodology (Allan et al., 2013a) could be combined with in vitro tissue-immersed techniques (Jahnke et al., 2011; Jin et al., 2013) and extended to wild organisms at various trophic levels to investigate trophic transfer and magnification on an equilibrium concentration in polymer basis. This would allow to convert concentrations in monitored species to other levels or the EQS values to the specific species available.

Information from this type of passive sampling work can be valuable in a research context. But is it also important in a regulatory framework? Although the European Water Framework Directive has or had a focus on water it also provides the opportunity to use matrices other than water (e.g. biota or sediment) for monitoring very bio-accumulative compounds; provided they can supply evidence that an equal level of protection of aquatic life was being achieved. For these substances, biota was the preference for chemical monitoring. The clear advantage of using biota in chemical monitoring over water is that biota accumulates hydrophobic compounds over quite a long time to levels in tissues that are more easily quantifiable with available analytical methods. Pollutant concentrations in tissue may provide a direct measure of actual exposure. This

Figure 2. In vivo implantation passive sampling using tubing made of silicone rubber inserted in the cavity of brown trout (Salmo trutta) exposed in the Alna River (Oslo, Norway).

is indeed the case when substances are not metabolised by the organism. Use of biota for chemical monitoring, however, introduces natural variability (caused by variable size, age, sex, physiological conditions and trophic level of sampled organisms) into reported data, which complicates or in some cases precludes their spatial and temporal comparability. Moreover, the specific biota species required for chemical monitoring may not be available at some sampling sites or adequate conversion factors to the correct species are not available. In addition, monitoring of biota is economically (and practically) feasible only at low frequency. The combination low frequency and inherent data variability from chemical monitoring in biota may complicate the decision making based on such data.

A possibility to assess compliance with EQS_{biota} using passive samplers. Passive samplers can provide a reliable measurement of free dissolved concentration (C_{free}) of very bioaccumulative pollutants in water C_{free} is the most relevant

measure of organism exposure in water. Levels found in both passive sampler and biota are proportional to C_{free}, and this information can be utilised as the common denominator in compliance checking. Whereas the relation of C_s to C_{free} is relatively simple and can be characterised with a known uncertainty, in case of biota the relation between C_{biota} and C_{free} is much more complex (see above). To enable compliance monitoring with EQS_{biota} based on C_{free} measurements, it is necessary to derive the required compliance checking criterion, i.e. to back-calculate from EQS_{biota} to C_{free} concentration that provides an equivalent protection of aquatic organisms.

Further discussion

Previous sections already discussed another potential solution applying abiotic passive sampling methods In this case, for compliance assessment, passive sampling data can be converted to lipid-based concentrations for aquatic organisms at low level in the trophic chain. These values represent concentrations that may be found in biota at equilibrium with the dissolved water phase and may be used for comparisons with EQS values derived for biota when converted to appropriate lipid basis. This approach provides information on the possible bioconcentration of pollutants from water into aquatic organisms, with a low inherent variability (e.g. filter feeders such as mussels). It should be kept in mind that this information is based on simple physical partitioning, and thus it cannot take into account food chain transfer/biomagnification and metabolism. Such procedure thus mimics only the bioconcentration process in organisms not taking into account metabolism.

The above discussion is relevant for compounds that accumulate in organisms but many compounds are mainly present in the water phase and require water monitoring. Classical chemical monitoring in water may often suite the legal requirements but there are situations where passive samplers may close gaps depending on substance properties or the specific situation. When for example the quantification limit (LOQ) of the classical method is higher than the environmental quality standard (EQS) and thus compliance cannot be legally confirmed, the use of a passive sampling method that has a lower LOQ is a defendable alternative. In the case method LOQ + uncertainty does not exceed the EQS, compliance can be confirmed. Since passive sampling provides a measure of time-weighted average concentrations, it is well suited for compliance against EQS that are derived for protection against chronic exposure of organisms (e.g. annual average concentration EQS). Passive sampling can also be applied in situations when concentrations fluctuate and protection against acute organism exposure (expressed by maximum allowable concentration) is desired, e.g. in the assessment of plant protection products in small water bodies. Although the maximum peak concentrations from pollution events cannot be derived from passive sampling, the integrative character of passive sampling significantly reduces the risk of missing peak events in comparison with conventionally applied monthly spot sampling under regulatory monitoring. Passive samplers can very well help to identify potential areas of exceedance that can be then subjected to high frequency sampling (time and/or flow proportional automatic sampling).

Estimates of contaminant concentrations in water generated by passive sampling are for the freely dissolved phase and are therefore directly amenable to use for compliance checking for substances that are not too hydrophobic ($\log K_{OW} < 5$) with environmental quality standards that are set as whole water concentrations by the Water Framework Directive (WFD). Preferably, with passive samplers compliance should be checked against quality standards derived for free dissolved concentrations. Field-measured or empirical organic carbon-water partition coefficients, K_{oc} and K_{doc} can be applied to passive sampling-derived freely dissolved concentrations to account for particle and dissolved organic carbon-associated contaminant concentrations. Because of the natural variability of organic matter and related uncertainty of K_{oc} and K_{doc} values, the conversion has to be conser-

vative to make sure that the quality standard expressed for free dissolved concentration provides the same level of protection of aquatic life as (or even higher than) the original standard.

Screening for emerging substances of interest generally relies on the measurement of these chemicals in abiotic matrices but increasingly on the use of measurements in biota. In many cases, the fate and metabolism of these emerging substances in biota is unknown and this can render the translation to exposed concentrations difficult. Exposure assessment in these conditions is not sufficiently robust. Consequently, passive sampling can be used to complement biota monitoring to strengthen exposure assessment. If monitoring is undertaken with (locally caught) caged organisms (e.g. fish), these can be implanted with passive sampling tags made of a similar polymeric material as that used in parallel for sampling water. This way, fish-water ratios can be estimated using identical absorptive phase in two distinct environmental compartments and could be complemented by measurement of $K_{lip\text{-}s}$ for these emerging substances.

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