

Theme Session J – Applications of passive sampling devices in environmental monitoring, assessment, research and testing

Conveners: Foppe Smedes (the Netherlands) and Ian Davies (UK)

The development of passive sampling devices for marine applications has been followed over the past few years by MCWG, WGBEC, and (particularly) WGMS. All of these groups have recognized the high potential of these techniques to directly address the availability of organic (and inorganic) contaminants in water and sediment. The technology and theoretical understanding has now reached a stage where application to environmental concerns arising from chemical contaminants/pollutants can be addressed with a degree of confidence.

Sixteen oral presentations were made at the Theme Session. The topic areas mentioned in the original Theme Session synopsis – passive sampling materials, use of passive samplers in water and sediment, use of passive samplers in conjunction with toxicity tests or biological effects measurements, applications in field surveys and to environmental risk assessment – were all represented in the contributions.

The papers presented in the Theme Session can be considered in 4 groups, related to the theoretical background to passive sampling, field applications of passive sampling in sediment, application of passive samplers in toxicity testing and related studies, and the outcome of the ICES Passive Sampling Trial Survey 2006–2007.

a) Theoretical background

Foppe Smedes gave an initial brief introduction to passive sampling, indicating that they offer the opportunity to obtain a measure of the activity of contaminants in the environment. Kees Booij (J:05) reviewed the range of samplers that have been used in water, with emphasis on hydrophobic contaminants. He discussed equilibrium and non-equilibrium sampling and the associated mathematics of uptake. The control of the kinetics of uptake of contaminants by passive samplers is exerted through diffusion processes in the sampling phase and the surrounding water phase (as well as the partition coefficient between sampler and water). Booij emphasised the need to estimate sampling rates of passive samplers in water to be able to calculate concentrations, and showed a modelling approach that simultaneously used data from several performance reference compounds to estimate sampling rate.

Tatsiana Rusina (J:08) took up this theme and described different approaches that have been used to directly measure sampling rates. Most of these require the difficult measurement of concentrations of contaminants in the water phase. She described a new experimental approach in which the concentration in the water phase in an aquarium is buffered by a large surface area of spiked silicone rubber sheets. Then unspiked sheets were suspended in the body of the aquarium to measure uptake profiles. The initial experiment demonstrated the importance of preventing loss of contaminants through evaporation, and the need for sufficient stirring in the aquarium. A further experiment is in progress and should clarify the relationship between sampling rate and hydrophobicity for silicone rubber. Rusina addressed another aspect of the properties of potential sampler materials in a poster (J:21) on diffusion coefficients.

Foppe Smedes (J:07) reviewed approaches to the use of passive samplers in sediment. He emphasised the ability of passive samplers to enable estimation of a measure of the activity of hydrophobic contaminants in sediment, and also the proportion of the total contaminant load in sediment that was available for release to the aqueous phase within a period of around 3 weeks. The remainder could be considered effectively unavailable. The sorption of contaminants in the available portion showed often similar partition coefficients as contaminants added to the sediment, for example as Performance Reference Compounds.

Passive samplers can also be applied to inorganic substances. Oddvar Royset (J:16) described several applications of DGT samplers with Chelex resin sorbants for metals, and ferrihydrite for phosphate, selenate and arsenate. Manganese dioxide disks can be used for radium in produced water. His group has demonstrated correlation between DGT data and effects data (gill function) in salmon in fresh water, suggesting that DGT collects the toxic fraction of, particularly, aluminium. DGT can also be applied in probe form in sediment, for example to study diffusive release of metals from contaminated sediment. Probes can be used to determine the effectiveness of capping (different materials, or depths) contaminated sediment.

b) Field applications of passive samplers in sediment

The environmental significance of hydrophobic contaminants in sediment has been a long-standing problem in marine environmental assessment and environmental management. Passive samplers offer the potential to directly measure the partition coefficients of hydrophobic contaminants between sediments and biota or water phases. Partition theory, which applies to most hydrophobic contaminants, indicates that the free dissolved concentration in the water-phase is considered to be the driving force for diffusive transport of contaminants and also for the uptake of the contaminants by aquatic organisms. A series of papers described the application of passive samplers in contaminated sediment.

Kristoffer Naes (J:06) described field studies in fjord sediments contaminated by coal tar pitch from aluminium smelters. He linked passive sampling, mainly using POM, with uptake of PAHs by *Hinia*, *Nuculoma* and *Nereis*. Uptake was not well modelled by the classical Karickhoff equation – the contaminants were much less (1–2 orders of magnitude less) available than predicted. Modelling based on bioaccumulation factors calculated from passive sampler data was much more effective in predicting concentrations in *Hinia* and *Nereis*. Lack of good fit for *Nuculoma* was thought to be the result of contamination of *Nuculoma* by sediment in the gut.

Kyari Yates (J:01) described a parallel project using sediments from Scotland that had also been contaminated by PAHs from an aluminium smelter. Concentrations in sediment greatly exceeded OSPAR BCs and BACs. Concentrations in pore waters sampled by silicone rubber decreased away from the smelter discharge. In general, the water extractable fractions of individual PAHs were 5–50% of the total concentrations. Koc values generally exceeded Karickhoff predicted values by approximately one order of magnitude. Both these papers emphasised the low proportion of the PAHs in the sediment that were available to take part in partitioning with aqueous and biotic phases within periods of up to 3 weeks. He supported this work with a poster (J:17) on the availability of PAHs in contaminated sediment from Vefsnfjord to infaunal worms.

Arto Sormunen (J:12) provided a link with the EU Modelkey project, and linked POM passive sampling data with uptake of contaminants by biota from spiked river sediments. Correlation with pore water concentrations from POM samplers was good for some compounds, but less good for others. Uncertainty in partition coefficients or other compound-specific factors, or differences arising from behaviour of the test organisms, may be significant.

Jarkko Akkanen (J:14) described the experiences of his laboratory in the use of Tenax to estimate bioavailability of contaminants in sediment. While the method was useful in general terms, they had experienced considerable difficulties in detail in linking extractable material in different availability fractions with uptake by test organisms. It showed that better understanding is required of the meaning of the amounts sorbed by Tenax in relation to uptake by organism. Further complications were reported linked to temperature, nutritional quality of the sediment, and ecological factors such as behavioural aspects of the test organisms.

Celine Tixier (J:10) has used LDPE to study the diffusive release of hydrophobic organic contaminants from sediment (in Thau lagoon), through measurement of freely dissolved concentrations of contaminants in pore water and overlying water. The measurements indicated that sediment acted as a diffusive source of CBs and heavier PAHs. Kyari Yates (J:13) continued the theme of management of contaminated sediment and reported concentrations of PAHs in pore waters of dredge spoils from various locations in Scotland. Data suggest that site specific assessment is required to allow for proportion of tightly bound PAHs.

Initial steps are being made in the integration of passive sampling devices with other oceanographic instrumentation. In a poster, Scott Carr (J:19) described an imaging and sampling system linked on a benthic lander for precise positioning of samplers in sediments, and the use of extracts of samplers in chemical analysis and toxicity tests.

c) Application of passive samplers in toxicity testing and related studies

Spiked passive samplers can be used to buffer or regulate the concentrations of hydrophobic contaminants in testing systems. A system of this type was described in contribution J:08 above to measure fundamental properties of samplers. However, the same system loaded through equilibration with water or sediment, can be used to provide controlled exposure concentrations in toxicity tests. Alternatively, extracts from passive samplers applied in water or sediment can be used as sources of toxicants for *in vitro* bioassays. This approach could be used to detect the presence of new chemicals in areas selected for such monitoring, or be used in combination with TIE systems to identify the cause of toxicity.

Marion Nipper (J:09) briefly compared the use of direct toxicity tests on sediment samples, with the faster and less costly tests that can be done on isolated pore water. However, the latter omits the potential for sediment to replenish contaminant burdens in pore water following absorption by test organisms. Her group use LDPE passive samplers to mimic available contaminants from sediment, and use these samples as source of contaminants for copepod and sea urchin gametes toxicity tests.

Partick Roose (J:11) described the increasing breadth of use of passive sampling in the new INRAM project in Belgian coastal waters. The project will link classical chemistry with passive sampling, bioaccumulation and biological effects measurements, leading into a risk-based approach to environmental assessment and environmental management. One component of the project will be the use of passive samplers as sources of contaminants for subsequent bioassays.

The ability to make comparable measurements of the activities of organic contaminants in different environmental phases has been used by Eric Morgan (J:15) to investigate seasonal changes in the activity of CBs in air, surface water and bottom water in Narragansett Bay. These were then related to seasonal changes in CB concentrations in fish (cod) and conclusions drawn regarding the likely sources and uptake processes (bioaccumulation vs biomagnification) leading to the observed burdens in the fish.

d) The ICES Passive Sampling Trial Survey 2006–2007

During 2006–2007, ICES WGMS and MCWG had collaborated on a field trial of the use of passive samplers, particularly silicone rubber, in water and sediment. Twelve laboratories from ICES countries (and one from Australia) joined the project. The primary target analytes for the project were polycyclic aromatic hydrocarbons (PAHs) and chlorobiphenyls (CBs). The final three papers of the Theme Session were devoted to this project, covering the design and organization of the project (Ian Davies, J:02), intercalibration aspects (Ton van der Zande, J:03) and the results treated as a field survey (Foppe Smedes, J:04), supported by a poster on the significance of biofouling of samplers (Lucia Vinas, J:18).

The preparatory work to gain commitment from participants, prepare a protocol for the trial, prepare materials for deployment in the field, and distribute them to the laboratories closely followed the projected timetable from April to September 2006 (J:02).

Deployment of samplers in the field was planned to begin in early October, but was delayed in some laboratories with the final deployment occurring on 10 November. This delay was inevitably reflected in later aspects of the project, i.e. the sending of samples to the central laboratory for analysis, analyses in-house and by the central laboratory, and the reporting of data to the coordinator. All analyses were completed by the end of April 2007.

Intercomparison of data for passive sampling of both water and sediment using silicone rubber was achieved through the PSTS programme for the 13 participating laboratories (J:03). The data cover both the measurements of freely dissolved concentrations of PAHs and CBs in water and sediment pore water, and the estimates of sampling rates of samplers in water. Data enable each laboratory to identify its performance in relation to both the reference laboratory and the other participants.

The data from PSTS and other sources have been combined to give an initial indication of the dominant sources of variability in the results from passive sampling in water. The priority areas for improvement are the analytical variance between laboratories, and also the selection and analysis of Performance Reference Compounds. Other aspects of the process, such as the spiking of sampler sheets with PRCs, and blanks, transport of samplers, and the between sampler variance in the field are relatively unimportant sources of variance.

The PSTS programme has provided new information on the distribution of freely dissolved CBs and PAHs in water and sediment pore water over a wide geographical range (J:04). The broad features of the distributions of CBs and PAHs are interpretable in terms of current general understanding of the sources, transport mechanisms, and environmental chemistry of CBs and PAHs.

Environmental validation of passive sampling of water has been provided through parallel analyses of mussels. Bioconcentration factors linking concentrations in mussels with freely dissolved concentrations in water determined by passive sampling showed strong correlation with K_{OW} values, and closely matched a published model of the bioconcentration of organochlorine compounds in mussels. Similar results were reported covering a period of 6 years in near shore waters of the Netherlands (J:19).

Freely dissolved concentrations in sediment pore water were used to calculate apparent sediment organic carbon – water partition coefficients (K_{OC}). K_{OC} values from passive sampling were correlated with K_{OW} values. Assuming that deviation from the Karrickhoff relationship indicates the unavailable portion, the data suggest that while most of the CBs present in the sediment are potentially available to the water phase, most of the PAH (>90%) are not available to take part in partitioning with water or organisms.

Passive samples of water were used to provide new data on the distribution of freely dissolved concentrations of some priority organic contaminants – data that would otherwise be difficult to obtain. Data are reported for lindane, chlorpyrifos, endosulphan-1, trifluralin, BDE047 and BDE099.

Principal Component Analysis of passive sampling data for freely dissolved contaminants in water demonstrated that sites showing different patterns of CB congeners or PAH compounds grouped together. The groupings could be interpreted in terms of differences in sources of contaminants experienced at different sampling locations.

Conclusions

Passive sampling enables environmental scientists, for the first time, to estimate the activities of hydrophobic organic contaminants (and some hydrophilic contaminants) in water and sediment. Previously, we have had to rely upon analysis of operationally-defined particulate and dissolved phases in water samples, knowing that the truly dissolved component was generally not accessible to our analytical techniques.

Well-chosen passive sampler, or reference, phases can act as sources of contaminants in toxicity testing and effects studies. Previously, the maintenance of constant dissolved concentrations, or activities, of hydrophobic substances in test systems has been extremely difficult, and exposure concentrations have been subject to systematic errors through sorption of the toxicants by both test organisms and the surfaces of the experimental system. The data underlying today's quality standards for water have been derived from systems that result in a proportion of the test contaminant becoming bound to dissolved organic matter, or suspended particulate material. Quality standards derived from systems that can maintain fixed concentrations of contaminants in solution, and for use in the interpretation of passive sampler data, are likely to be different from those currently in use. The ability to reliably maintain test concentrations may require us to review our views of the relative and absolute toxicity of environmental contaminants.

As activity is the driver of environmental impact of contaminants, the use of passive samplers should lead to improvements in environmental status assessment. Status assessments will be able to take availability of contaminants into account, and lead to better assessments of environmental risk. Consequently, environmental managers and regulators will have better, more directly relevant, information on which to base their decisions.

The ICES PSTS 2006–2007 project has demonstrated the reliability of the distribution, use and analysis of silicone rubber passive samplers. The unique data obtained offer new perspectives on contaminant distribution and availability. The increasing introduction of passive samplers into routine environmental monitoring and assessment should lead to their adoption as components of international monitoring programmes, for example under OSPAR or HELCOM. ICES should seek to encourage this development, both through expressing support for, and promoting, relevant science, and noting the opportunities presented by passive sampling in advice to the Commissions.