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Report of the Workshop on the Application of Passive Sampling and Passive Dosing to Contaminants in Marine Media (WKPSPD)

29–31 January 2013

Copenhagen, Denmark



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Executive summary

The ICES Workshop on the Application of Passive Sampling and Passive Dosing to Contaminants in Marine Media (WKPSPD) met at ICES Headquarters, Copenhagen, on 29–31 January 2013. The meeting was co-chaired by Kees Booij (the Netherlands) and Craig Robinson (UK), with 16 other participants from 8 countries. The main aims of the workshop were to report on the current state of the art for passive sampling (PS) and passive dosing (PD), and to identify opportunities and gaps with respect to their use in environmental monitoring and assessment programmes required by Regional Seas Conventions, or the EU Marine Strategy Framework (MSFD) and Water Framework Directives (WFD).

The Workshop was organised around 5 theme sessions each with presentations and discussions on identifying where PS/PD is able to meet the requirements of OSPAR and EU monitoring programmes, what the important knowledge gaps are, and how further progress can be made. The report is also structured around these themes, with an over-arching discussion. The five themes were:

- Technical requirements of compliance monitoring for OSPAR and under EU Directives
- Passive sampling of marine and transitional waters
- Passive sampling of sediments
- Linking passive sampling to biota concentrations
- Passive dosing in toxicity tests

The Workshop recognised that the most mature use of PS is for hydrophobic contaminants, whilst uncertainty around sampling rates means that PS for polar compounds (although useful in investigative monitoring) is not currently suitable for compliance monitoring. There was a lack of available expertise regarding PS of metals. However, it was recognised that there is a long history of passive metal sampling in both water and sediments, that the approach is more mature than PS for polar compounds, and that the concentrations determined have toxicological relevance.

PS is used to determine the chemical activity of environmental contaminants (sometimes described as “pollutant pressure”) through measuring their freely dissolved concentrations (C_{free}). Since C_{free} of hydrophobic compounds is proportional to concentrations in biota (C_{biota}), it is directly linked to toxicity, requires no normalisation for global comparability, and is a more relevant metric for environmental assessments than are “total” concentrations in water or sediments that do not relate well to toxicity (even if normalised, e.g. for amorphous organic carbon).

The Workshop identified several key weaknesses of existing monitoring that can be addressed by PS. For biota, traditional monitoring is hampered by the diversity of organisms employed, and physiological variability in response to environmental variables; this complicates comparisons between regions, or against EAC/EQs. Like organisms, PS devices (PSDs) accumulate contaminants over time, to similar concentrations, and with similar drivers for uptake. However, PS has negligible background concentrations, the derived C_{free} is not influenced by environmental conditions, and PS allows global comparisons. Furthermore, PS measures what organisms are exposed to (including metabolisable compounds) and not only what bioaccumulates. PS therefore has the potential to replace biota monitoring for hydrophobic compounds, although additional biota monitoring could still be required to assess the risks of secondary poisoning, including exposure to humans. Replacing existing con-

centration trend monitoring in biota by PS would require both techniques to be operated in parallel for some time in order to link previous biota based time series to PS based trend monitoring.

For water, time-integrative sampling by PS improves upon spot sampling and provides much lower detection limits. An issue identified for offshore water PS programmes was a shortage of suitable sampler attachment sites (e.g. buoys, tripods) and an alternative could be the use of on-ship, ferrybox-style, PS systems. For sediments, PS measures the pore water C_{free} directly, providing better linkage to toxicity than traditional “total sediment” concentrations.

PS of hydrophobic contaminants does not currently meet all OSPAR/EU technical requirements (e.g. guideline documents, assessment criteria, proficiency testing and QA/QC procedures). However, ways forward were identified, and in some cases instigated by the Workshop. It was noted that accurate sampler-water partition coefficients are crucial for a successful use of PS in monitoring programmes. For assessment purposes, EAC/EQS values should be defined in terms of C_{free} . Due to the proportionality between C_{free} , C_{biota} and toxicity, the same values could be applicable for both water and sediments (pore water).

PD was identified as an appropriate technique for generating aquatic toxicity data required for deriving EAC/EQs expressed as C_{free} . The option of replacing the use of EAC/EQs in assessing hydrophobic compounds with a programme based on PS and subsequent PD in bioassays was considered premature, although including assessments of hydrophobic mixture effects would be informative within an integrated assessment.

Recommendations from the Workshop include the addition (for hydrophobic contaminants) of sediment and water PS to the OSPAR pre-CEMP; derivation of assessment criteria; production of guidelines by ICES Expert Groups (WGBEC, MCWG, WGMS); initiation of a proficiency testing development exercise by QUASIMEME; further development of QA/QC procedures; and the development of guidelines for the measurement of sampler-water partition coefficients, in order to reduce uncertainty around the available values and thus on the C_{free} values obtained.

1 Glossary

BAC	Background Assessment Concentration. Statistically defined concentration, used by OSPAR to assess whether environmental concentrations are close to background
C_{free}	Freely dissolved aqueous concentration
DGT	Diffusive Gradients in Thin films. Passive sampler mainly used for metals
EAC	Environmental Assessment Criteria. Threshold concentration used by OSPAR to assess whether environmental concentrations may cause significant environmental harm
EQS	Environmental Quality Standard. Threshold concentration under the WFD that is designed to protect the most sensitive species from significant harm
HOCs	Hydrophobic organic contaminants
K_{sw}	Sampler-water partition coefficient
LDPE	Low density polyethylene.
PDMS	Polydimethylsiloxane.
POCIS	Polar Organic Chemical Integrative Sampler
POM	Poly(oxyethylene)
PRC	Performance Reference Compound. Substance that is not found in the environment and which is spiked to passive samplers prior to use. Used to model uptake of target analytes by the sampler.
PS	Passive sampling
PSD	Passive sampling device
PTS	Proficiency Testing Scheme
SPMD	Semipermeable Membrane Device. Passive sampler using lipid within a membrane to sequester hydrophobic contaminants
SPME	Solid phase microextraction
SR	Silicone rubber. Sampler material used as sheets or strips. Composed mainly of PDMS
VOCs	Volatile organic compounds

2 Opening of the meeting

The Workshop on the Application of Passive Sampling and Passive Dosing to Contaminants in Marine Media (WKPSPD), co-chaired by Craig Robinson, UK, and Kees Booij, NL, met at ICES Headquarters, Copenhagen, Denmark, 29–31 January 2013. Claus Hagebro and Vivian Piil of ICES welcomed the participants and wished them a successful meeting. The participants introduced themselves and their affiliations (Annex 1) and described their specific interests within the field of passive sampling and passive dosing.

The meeting was divided into 5 sessions (compliance monitoring, passive sampling of water, passive sampling of sediments, passive sampling in relation to biota concentrations, and passive dosing), each consisting of a series of presentations followed by discussion around the topic, with the view of making recommendations in respect of the Terms of Reference (ToRs).

3 Adoption of the agenda

The agenda (Annex 2) based on the ToRs (Annex 3) that had been drafted by the Advice Drafting Group for Monitoring (ADGMON 2012) and approved by the Steering Group on Human Interactions on the Ecosystem (2012/2/SSGHIE 01) was adopted.

4 Session 1: Compliance monitoring

This session was intended to discuss where passive sampling fits into current frameworks of contaminant monitoring in the marine environment, including potential advantages from passive sampling over conventional approaches.

In detail, it was intended to identify the requirements of the policy drivers for monitoring and assessment of environmental contaminants, investigate where passive sampling meets or does not meet these requirements, and how to progress the technique towards satisfying those requirements.

Compliance monitoring of offshore and coastal waters is required under the European Marine Strategy Framework Directive (MSFD)(EU, 2008a), whilst the Water Framework Directive (WFD) (EU, 2000) requires compliance monitoring be undertaken in coastal and transitional waters; additionally, monitoring to allow environmental status assessments is required for the OSPAR Coordinated Environmental Monitoring Programme (CEMP) (OSPAR, 2008; OSPAR, 2010).

4.1 Presentations

4.1.1 Paul Whitehouse (by WebEx): "EQSs for controlling toxic substances under the Water Framework Directive: challenges in implementing biota standards"

The Water Framework Directive (WFD) requires Environmental Quality Standards (EQS) to be set for toxic substances and these standards are used as regulatory tools to monitor and control releases to the environment. Some of the new EQSs for Priority Substances developed under the WFD are expressed as concentrations in the body tissues of animals rather than in environmental matrices such as water or sediment. In principle, an approach based on biota standards is sensible for highly lipophilic and bioaccumulative substances. However, there are real technical challenges to the implementation of these biota standards, particularly to establish monitoring regimes that will provide reliable information about the risks to biota, and trends in chemical exposure.

Experience in the UK and elsewhere highlights serious concerns about relying on wild caught native fish as the basis of compliance assessment, e.g., the availability of material for sampling, high levels of variability (leading to the need for large sample sizes) and animal welfare issues. There is a high risk of inconsistency in approach (and potential bias) between Member States resulting from differences in their approaches to the implementation of biota standards.

There are a number of possible approaches to assessing compliance with biota standards:

- 1) Sampling tissues from wild-caught biota
- 2) Sampling tissues of caged biota
- 3) Passive sampling as a direct 'surrogate' for biota
- 4) Back-calculation of biota EQSs to an equivalent water concentration (and compliance assessment based on analysis of water samples)
- 5) Back-calculation of biota EQSs to an equivalent water concentration (and compliance assessment using passive sampling of water to overcome analytical sensitivity problems)

The UK commissioned a programme of research in 2011-12 to examine different options for assessing compliance with biota standards. This research involved parallel

deployments of caged biota alongside passive sampling devices (PSDs), water sampling and sampling of 'wild caught' fish at a range of locations in the UK. This showed that caged biota and PSDs can pick up a range of priority compounds but that direct water sampling failed to detect most of the compounds of interest. PSDs could form part of a monitoring strategy that reduces reliance on collection of 'native' fish. At present, the evidence for using PSDs as direct surrogates for fish is not persuasive, but further research into the role of PSDs is warranted.

4.1.2 Peter Lepom: "Passive sampling in regulatory monitoring – Opportunities and limitations."

The presentation provided an overview of monitoring tasks and monitoring requirements resulting from European legislation including Water Framework Directive (2000/60/EC) (EU, 2000), Directive on Environmental Quality standards (2008/105/EC) (EU, 2008b), Commission Directive on technical analysis for chemical analysis and monitoring of water status (2009/90/EC) (EU, 2009a), Marine Strategy Framework Directive (2008/56/EC) (EU, 2008a) and Commission Decision on Criteria for Good Environmental Status of Marine Waters (2010/477/EU) (EU, 2010a). At the moment, passive sampling devices (PSDs) are mainly applied in surveys aiming at identification of hot spots of contamination, reference sites, and new contaminants as well as at comparing concentration levels between different locations. Authorities have not used PSDs for compliance checking with environmental quality standards (EQSs) primarily since uncertainties in transferring concentrations measured in the sampling phase into freely dissolved water concentrations are considered too high. Another issue which needs to be addressed when using PSDs for compliance monitoring is the fact that EQSs refer to total and not to freely dissolved concentrations. The use of PSDs in temporal trend monitoring seems to be a promising approach; however, so far there is little practical experience in this field of application.

4.1.3 Martin Mørk Larsen: "Passive sampling and the monitoring requirements of OSPAR and HELCOM."

This presentation summarised the history of PS in an OSPAR context (reports of Contracting Parties using PS, and the interest in the ICES Passive Sampling Trial Survey (PSTS)). It noted that monitoring under the OSPAR Coordinated Environmental Monitoring Programme (CEMP) requires three things to be in place: guidelines (e.g. ICES TIMES document), QA procedures (e.g. proficiency testing), and Assessment Criteria (e.g. Background Assessment Concentrations and Environmental Assessment Concentrations). The OSPAR combined Working Groups on Monitoring and on Trends and Effects of Substances in the Marine Environment (MIME) has also indicated a desire to see a new project with the aim of investigating ways in which PS can improve monitoring for CEMP and MSFD purposes. OSPAR/HELCOM require advice on how to integrate data from PS with existing sediment, biota and biological effects monitoring and on how PS can be used in integrated monitoring of contaminants and biological effects.

4.1.4 Uta Kraus: "Testing and validation of passive samplers for monitoring priority organic pollutants for WFD, MSFD, HELCOM and OSPAR."

The applicability of two PSDs – silicone rubber sheets (SR) and LDPE membranes – for the monitoring of 73 organic pollutants (PAHs, PCBs, halogenated and polar pesticides, PFASs, fire retardants, pharmaceuticals; log_{K_{ow}} values from -0.21 to 8.85) in coastal and marine environments was tested under real-world conditions. This included logistical issues as well as the development of PSD extraction procedures for

both polar and non-polar compounds. To characterize the zones of tidal-influenced river, coastal sea and open sea, three sampling sites at the Elbe River (Hamburg Harbour), in the Fehmarnsund fairway (Baltic Sea) and offshore of Helgoland (North Sea) were chosen. PSDs were deployed between May 2010 and September 2011 with exposure times ranging from 33 to 83 days. A light-weight modular deployment cage was constructed which allowed the simultaneous deployment of different PSDs. By the use of 13 performance reference compounds (PRCs, $\log K_{ow}$ range 4-9), the calculation of time-weighted average concentrations (C_{TWA}) was carried out and results from passive samplers were related to those of conventional sampling methods. The study aimed to contribute to the characterization of various PSDs in their usefulness as monitoring tools for hazardous organic substances in marine and coastal waters regarding practical handling and performance and to assess their capacity as complementary monitoring tools for marine monitoring.

Lessons learned:

- Long-term regular deployment periods for PSD are difficult to accomplish in marine environments
- Both sampler types (SR, LDPE) withstand sea conditions without the support of a closed cage, allowing for freely moving sampling devices that are less prone to biofouling than fixed ones
- An extraction protocol was introduced that allows the parallel extraction of polar and nonpolar compounds in one single sample.
- Up to 72 substances were detected in silicone rubber sheets (max. 69 substances were found in a single sample). LDPE membranes detected exclusively non-polar compounds in both coastal and marine waters in reliable fashion.
- Estimated C_{TWA} values for hydrophobic substances showed generally good agreement with concentrations determined in conventional unfiltered 100L water samples (less than a factor of 10 difference). PRCs seem to compensate successfully for changing environmental conditions (e.g. biofouling) and long deployment periods despite the total loss of three PRCs with $\log K_{ow}$ values <5 (Fluorene-D10, Phenantrene-D10; PCB 10) during even the shortest deployment times.

4.2 Discussion on compliance monitoring (WFD) and status monitoring (OSPAR)

Drivers. The key drivers in compliance monitoring of marine, coastal and transitional waters are the OSPAR CEMP (OSPAR, 2008; OSPAR, 2010), the MSFD (EU, 2008a), and the WFD (EU, 2000), particularly the daughter Directives on Environmental Quality Standards in the field of water policy (EQS Directive; EU, 2008b) and on Technical Specifications for Chemical Analysis and Monitoring of Water Status (QA/QC Directive; EU, 2009a), which are also applicable to future monitoring undertaken for the MSFD. WFD Technical Guidance Documents 19 and 25 state that passive sampling can be used as a complementary technique for surveillance, operational, or investigative monitoring of both waters and sediments (EU, 2009b; EU, 2010b). The WFD also states that Member States can use alternative matrices for compliance monitoring, but to do so then they must define and use EQS values that are at least as protective as those specified in the EQS Directive. EU and OSPAR define threshold concentrations that provide adequate protection of aquatic systems.

These are named Environmental Quality Standards (EQS) within the WFD/MSFD and Environmental Assessment Concentrations (EAC) within OSPAR.

Comparability of PS data with EQSs and OSPAR assessment criteria. The EU presently suggests passive sampling as a complementary method for investigative monitoring in cases where concentration thresholds are exceeded (EU, 2009b; EU, 2010b), but not for surveillance monitoring and operational monitoring, where compliance with EQSs need to be demonstrated. The EQS guidance document states that the standard laboratory toxicity and bioconcentration tests contain low levels of total organic carbon (TOC) in the test system, and hence, the resulting EQSs refer to dissolved concentrations (EU, 2011). It follows that compliance assessment with a water column EQS should ideally be based on the sampling and analysis of the dissolved fraction. In contrast, the EQS directive 2008/105/EC stipulates that the EQS for organic compounds refer to “total concentrations in the whole water sample”, albeit without further justification (EU, 2008b). Member states may opt for compliance checking against a biota- or sediment-based EQS if it can be shown that these EQSs are at least equally protective as the whole water based EQS. The EACs used by OSPAR are primarily based on aqueous toxicity data that have been recalculated to concentrations in sediments and biota using equilibrium partitioning models (OSPAR, 2004); OSPAR requires monitoring of biota and sediment matrices (rather than water) for contaminants which accumulate through the food chain but which cannot easily be detected in seawater due to their low concentrations (OSPAR, 2009).

Quality Assurance. OSPAR and EU prescribe a number of criteria for laboratories and sampling methods to ensure that valid and comparable data are generated within monitoring programs (OSPAR, 2008; EU, 2009a) (Table 1). Methods should be documented and validated, and laboratories should have a quality assurance and control system in place to monitor and control data quality; for the WFD procedures should be in accordance with EN/ISO/IEC 17025. Reference materials should be used, and laboratories should participate in proficiency testing schemes for the analytes of interest. Minimum performance requirements for chemical methods used in WFD monitoring are that the measurement uncertainty be smaller than 50% at the level of the EQS, and that the limit of quantification is equal to or less than 30% of the relevant EQS (EU, 2009a). This implies that passive sampling based monitoring should be subject to the same QA/QC measures as the monitoring of sediments and biota, including methods to estimate accuracy and precision. A further OSPAR requirement is that background assessment concentrations for the sampled matrix be available.

Background Assessment Concentrations (BAC) for the OSPAR monitoring programme are available for biota and sediments, while no criteria exist for water. MCWG will be requested to derive BACs in water. This requires an assessment of aqueous concentrations in remote areas, and several WKPSPD participants indicated a willingness to supply such data.

Concentration basis of EQSs. Water monitoring of hydrophobic contaminants under the WFD is, however, based on whole (unfiltered) water samples, while passive sampling yields freely dissolved concentrations. WKPSPD notes that the EU guidance document recommends that water EQS be defined in terms of concentrations of dissolved contaminants (EU, 2008b) and supports this recommendation.

Guidelines have been published for the sampling of hydrophobic compounds in water using silicone rubber (Smedes and Booij, 2012). This guideline could be extended relatively easily to include other polymers. A guideline for passive sampling

of sediments is in development (WGMS, 2007). For other environmental matrices, OSPAR has a general guideline for each matrix (e.g. analysis of contaminants in sediment) and technical annexes for the compound groups to be measured in this matrix. It was discussed that the same approach could be useful for passive samplers, considering that analytical methods might differ more between samplers than between compounds and that references to analytical methods in existing guidelines should be sufficient.

No **proficiency testing schemes** (PTS) exist for passive sampling, but intercomparison exercises have been conducted. In order to establish a PTS, a sufficiently large number of laboratories will have to participate, probably around 10. It was discussed how a PTS would have to be organized to take into account variability at different levels. If a passive sampler is provided for analysis, the PTS will give information about the variability between the laboratories' analytical methods. This approach would be comparable to present PTS on biota or sediment. Additionally, the calculation step for calibration of sampling rates (converting concentration/sampler into water concentrations) could be assessed by sending nominal data to participants.

A PTS could be built up similarly to QUASIMEME's development exercises, which start with assessing individual steps of the analytical procedure and are adjusted as more information emerges.

A network of PTS providers (PT-WFD) should be informed about interest in a passive sampling PTS, for example through QUASIMEME or ICES MCWG. QUASIMEME have been invited to visit the MCWG meeting in March where the question of PTS on passive sampling could be discussed further. However, it is important that requirements and expectations regarding the technical content of a PTS are stated clearly by WKPSPD.

Table 1. Key requirements of OSPAR and EU for chemical monitoring.

REQUIREMENTS	REQUIRED BY		PRESENT STATUS FOR PASSIVE SAMPLING
	OSPAR	EU	
Guidelines PS in water	x	x	available for SR (Smedes and Booij, 2012) not available for LDPE, but could be derived from guideline for SR without too much effort. available for SPMDs (Huckins <i>et al.</i> , 2006) available for DGT (www.dgtresearch.com) insufficiently available for POCIS insufficiently available for Chemcatcher
Guidelines PS in sediment	x		in development for SR (WGMS, 2007)
PTS scheme	x	x	in development
Certified Reference Materials	x	x	not available
Accuracy and precision assessment	x	x	General approach available for nonpolar samplers (Booij and Smedes, 2010) No methods available for polar samplers Unknown for passive metal samplers
Background Assessment Concentrations	x		Available for PAHs, PCBs, HCB, DDE (MCWG, 2013)
Environmental Assessment Criteria	x		In development
Environmental Quality Standards		x	Not available for C_{free} ; The forum for EQS development is the EU WFD Working Group E. OSPAR and ICES (through relevant expert groups) could advise.
ISO standard	x	x	ISO 5667-23:2011(E) (ISO, 2011)
QA/QS system in accordance with ISO 17025		x	not assessed by the workshop

Compounds measurable using passive sampling. Passive sampling methods are best developed for hydrophobic compounds, including PCBs, PAHs, PBDEs, HCB and HCB. It was unclear whether or not hexabromocyclododecane (HBCDD) had been analysed successfully using passive sampling. Based on its $\log K_{ow}$ value of 5.6, it falls into the range of compounds suitable for passive sampling, for example using silicone rubber. PFOS has not been tested sufficiently. It might not work with the same polymers as used for the hydrophobic compounds. Dicofol, heptachlor, heptachlor epoxide and dioxins were discussed, but very few results are available, if any. The capability of PSDs for measuring aqueous concentrations of organic contaminants has been demonstrated for most of OSPAR's list of chemicals for priority action and for the compounds listed in the EU's EQS directive at detection levels $< 10 \text{ pg L}^{-1}$ range for nonpolar contaminants (e.g. hexachlorobenzene, PCBs, PAHs, PBDEs) and $< 2 \text{ ng L}^{-1}$ for polar contaminants (e.g., diuron, simazine, chlorfenvinphos) (Mills *et al.*, 2011).

Virtually all trace metals can be sampled by Diffusive Gradients in Thin films (DGT) at detection limits of 10 ng L^{-1} and lower (DGT-Research, 2013). The interpretation of DGT derived metal concentrations is difficult, because both freely dissolved and labile complexes are taken up by the sampler. WKPSPD recognises the potential of DGT for monitoring of marine/estuarine waters (Dunn *et al.*, 2003; Forsberg *et al.*, 2006; Schintu *et al.*, 2010; Mills *et al.*, 2011) and sediments (Zhang *et al.*, 2002; Gillan *et al.*, 2012), and also recognises that relationships between DGT derived metal concen-

trations and bioaccumulation (Schintu *et al.*, 2010; Bade *et al.*, 2012) and toxicity (INAP, 2002; Simpson *et al.*, 2012). An in depth evaluation was however not possible within the available time.

Passive sampling techniques for polar organic substances are not sufficiently well developed for their use in compliance monitoring to be recommended (Section 5.2) although they are useful for investigative monitoring, where semi-quantitative information is often valuable. Whilst passive sampling techniques for volatile organic compounds (VOCs) exist (Section 5.2), these are typically applied to water samples in the analytical laboratory, rather than during field sampling.

PSDs vs. batch water sampling. Assessing the accuracy of PSDs for nonpolar compounds is a difficult task because of the experimental difficulties involved. Concentrations of hydrophobic compounds in water are extremely low and difficult to measure with alternative methods. Comparisons with filtration/extraction methods require large volumes of water to be extracted. The risk of contamination is high, and freely dissolved compounds cannot be completely separated from the particulate fraction due to sorption on filters and dissolved organic carbon carrying hydrophobic compounds through the filter (Hermans *et al.*, 1992). Still, Kraus *et al.* (section 4.1.4) observed that PSD-derived concentrations were within the same order of magnitude as concentrations in unfiltered batch water samples. Concentrations of PAHs obtained by passive sampling (Chemcatcher) and repeated batch sampling in the river Meuse agreed within a factor of 5 (Greenwood *et al.*, 2009).

Mazzella *et al.* (2010) observed a good correspondence between polar pesticide concentrations obtained from continuous water sampling and from passive sampling by POCIS. Kaserzon *et al.* (2012) report for perfluorinated carboxylic acids and sulphonamic acids from that concentrations obtained by passive sampling with a modified POCIS were 18% smaller than concentrations from repeated batch sampling.

PSD variability among labs and among samplers. Allan *et al.* (2009) showed that C_{free} values of nonpolar compounds obtained from LDPE strip samplers, SPMDs and silicone PSDs deviated less than a factor of 2 from the average of six PSDs. These authors speculated that this variability was due to uncertainties in the sampler-water partition coefficients, to analytical variability among laboratories, and to the use of different models for the compound dependency of the sampling rates. Similar results were reported by Miège *et al.* (2012) for an *in situ* intercomparison exercise on passive sampling of PAHs in surface water, organized by the French AQUAREF network. Recently, an interlaboratory study on passive sampling of emerging contaminants (e.g., polar pesticides, pharmaceuticals, PBDEs, steroid hormones) was organised by the NORMAN network. Preliminary results for BDEs identified chemical analysis and calculation methods (calculation errors and use of inappropriate models) as major sources of variance (Smedes, 2012), while the among sampler variability within individual laboratories was minor. The ICES Passive Sampling Trial Survey identified chemical analysis (20-40%) and sampling rate estimation (30%) to be the main sources of interlaboratory variability of reported C_{free} values of PAHs and PCBs (Smedes *et al.*, 2007b).

Standardization. Differences in C_{free} estimates among passive sampler types raises the question of whether standardisation of passive sampling methods is worth pursuing. In the short term, the use of a standard passive sampling polymer would improve comparability of results. However, polymer characteristics might be changed by the manufacturers and there should be room for new developments, e.g. new materials may become available or new compounds should be included. Standardisa-

tion of C_{free} estimation methods and sampler water partition coefficients and sampling materials may reduce interlaboratory variability, but hampers the improvement of accuracy, in case better calibration values and improved samplers become available. Further, the use of multiple passive sampling methods in PT schemes allows for a better assessment of each method's accuracy.

5 Session 2: Passive sampling of marine and transitional waters

5.1 Presentations

5.1.1 Els Monteyne: "The role of passive sampling in the Belgian monitoring program"

Monitoring of organic pollutants in the marine environment is costly and time-consuming. Many data-points need to be generated for spatial or temporal chemical assessment. The use of passive sampling (PS) to provide representative measurements of concentrations in water and sediments has received increasing interest by scientists and regulators during the past decade. Research conducted in the context of INRAM project (2007–2010) provided some clear indications (for PCBs and PAHs) that PS techniques may provide the link between freely dissolved concentrations and biological effects (Janssen *et al.*, 2010).

For 4 subsequent years polydimethylsiloxane (PDMS) passive samplers were deployed in the 3 major harbours in Belgium, and at sea. The sheets were analysed for PAHs and PCBs. With the use of the performance reference compounds (PRCs), sampling rates (R_s) were calculated and water concentrations were determined. The sampling rates were calculated using the non-linear least-square method, taking into account lower uptake rates for higher molecular weight compounds. R_s varied from 1 to 35 L d⁻¹ for the different target compounds, while estimated freely dissolved concentrations for sum 15 PAHs varied between 4 and 170 ng L⁻¹ and for sum 14 PCBs between 0.030 and 3 ng L⁻¹. The samplers showed a difference in pollution pressure between the harbours, as well as within the harbours. Contaminant pressure could also be defined by ng of compound per g of sampler. Although this would be a relative scale, when linked to toxicity, it could also become a meaningful figure. Taking sorption to organic matter into account, computed concentrations from passive sampling data to whole water concentrations give lower concentrations than the measured whole water concentrations. In Belgium, passive sampling in a reference station with other measuring devices is done the whole year around now.

5.1.2 Jan Brant: "Use of passive sampling devices for surveys and monitoring in UK waters."

In the UK, passive sampling using silicone rubber and POCIS has been used offshore in a one off survey to attempt to measure all organic compounds on the OSPAR and WFD priority lists (Balaam *et al.*, 2011). The main drivers for this survey were the implementation of the MSFD and the requirement for coherence between this Directive and the WFD in terms of the matrices and compounds measured, in coastal waters. The WFD states that sediment, biota AND water are sampled, but in the marine environment (mainly under OSPAR), there has previously been no requirement to measure water because of the inherent problems with obtaining sufficiently large sample volumes to achieve the very low limits of detection that would be required to quantify anything (let alone achieve EQS values), and the transient nature of the water and therefore its lack of representativeness to the surrounding area. The main UK marine policy customer (Defra) requested that a collaboration be undertaken between all of the UK agencies (Cefas, Marine Scotland Science (MSS), Environment Agency (EA), Scottish Environment Protection Agency (SEPA) and Northern Ireland Environment Agency, NIEA) in order to assess the capability of passive samplers for use in routine monitoring for this wide range of chemicals.

Table 2. Compounds analysed during the UK passive sampling survey.

GROUP	HAZARDOUS SUBSTANCE	CEFAS	EA	MSS	SEPA	NIEA
Volatile organic compounds (not by passive sampling)	Benzene					✓
Chlorobenzenes	Pentachlorobenzene		✓			
	Trichlorobenzenes		✓			
Chlorinated alkanes (not by passive sampling)	Chloroform					✓
	Dichloromethane					✓
	1,2-dichloroethane					✓
Dioxins and furans	PCDDs		✓			
	PCDFs		✓			
Pesticides/biocides	Pentachlorophenol				✓	
	Hexachlorobenzene				✓	
	HCHs				✓	
	Methoxychlor					
	Trifluralin				✓	
	Endosulfan				✓	
	Dicofol					
	HCBD				✓	
	Chlorfenvinphos					
	Alachlor					
PCBS	PCBs			✓		
PAHs	PAHs			✓		
Musk xylenes	Musk xylenes		✓			
SCCPs	SCCPs		✓			
Brominated flame retardants	TBBP-A	✓				
	PBDEs	✓				
	HBCD	✓				
Phthalates	DBP & DEHP		✓			

Alkylphenols	Octylphenol	✓
	Nonylphenol	✓
	Nonylphenol ethoxylates	
	2,4,6-tri- <i>tert</i> -butylphenol	
Metals and organometals	Organotins	✓
Pharmaceuticals	Clotrimazole	✓

The list of chemicals considered is listed in Table 2, along with the laboratory which ultimately would undertake the analyses. A few compounds were immediately ruled out as being unlikely to be successfully monitored using passive sampling due to their volatility, these were the VOCs (benzene) and chlorinated alkanes. These compounds were not considered further in this passive sampling programme. Of the remaining compounds, some were not routinely measured by any of the participating laboratories using a targeted method, and so were covered only by a screening method (GC and LC) carried out by the Environment Agency. These compounds were musk xylenes and short chain chlorinated paraffins, and these compounds were therefore not quantified (since no internal standards are used in the screening method). The samplers used were silicone rubber and POCIS.

The main outcomes of this project were:

Positive

- PCBs and PAHs gave good results with observable gradients, this was predicted since they had been analysed many times before in this matrix.
- Compounds with relatively low K_{ow} (e.g. azoxystrobin, $\log K_{ow}=1.58$) were sequestered by silicone rubber.
- Pesticides and biocides showed estuary specific 'fingerprints', so sources could in the future be tracked quite nicely.
- Alkylphenols were successfully measured at low levels and showed nice gradients from inshore to offshore.
- Dioxins were measured in the low pg L^{-1} level, although the internal standard recovery was very variable from sample to sample.
- Advances were made in the analysis of PBDEs after the first phase of sampling, which gave rise to coelution of internal standards from the many standards/PRCs in the mixture. This was resolved by additional clean up before analysis.
- New extraction methods were derived for organotin analysis (Smedes and Beeltje, 2011) following unsuccessful recovery of internal standards in the first phase of work.
- Partition coefficients were determined for 72 additional compounds in order to calculate water column concentrations (Smedes and Beeltje, 2010).
- Comparisons with mussels were in general quite good.

Negative

- One of our reference sites apparently had a VERY low sampling rate, leading to a calculation of relatively (and uncharacteristically) high concentrations.
- There were very few fixing points offshore suitable for attaching passive samplers to.
- Phthalates proved to be very difficult to measure due to their ubiquitous nature, leading to high background values.
- POCIS samplers were not analysed quantitatively due to lack of internal standards.

Major points from this work

- There are no fixing points offshore. We can resolve this by deploying lots of buoys/tripods, by towing samplers on vessels of opportunity, having fixed passive sampling stations on research vessels and other boats (analogous to the ferrybox), or by taking sediment samples and doing equilibrium sampling *ex situ*.
- Partition coefficients are still not available for PBDEs.
- Further validation work is required for dioxins, phthalates and organotins.
- If we are going to move to passive sampling, we need to cover all substances? For WFD this means that we have to include volatile compounds (chloroform, benzene, etc.).
- While passive samplers do not exactly mirror concentrations in mussels, neither do mussels exactly match concentrations in fish (or other types of biota), so we should look at this as an alternative matrix rather than a surrogate for a particular type of biota.
- No quantitative data can be derived for POCIS without some way of correcting for differences in sampling rates.

5.1.3 Ian Allan: The state of the art with polar samplers

The aim of Ian Allan's presentation was to provide an overview and current status of passive sampling for polar substances. These polar compounds are generally those with $\log K_{ow} < 3$ and include pesticides, pharmaceuticals and personal care products as well as ionised substances such as acidic herbicides. Polar (and ionised) substances are likely to be present in water/wastewater at higher concentrations than hydrophobic compounds. Owing to the nature of the sources of these chemicals, fluctuating concentrations can be expected as a result of their emission sources. A particular challenge for measurements in the marine environment is the low limits of detection needed in response to low environmental quality standards (EQS) and low expected concentrations in these waters (dilution from source).

Different devices have been developed over recent years to measure time-weighted average concentrations of these substances in water. The Polar Organic Chemical Integrative Sampler (POCIS) is composed of a particulate sorbent phase (either OASIS HLB or a triphasic mixture) sandwiched between two porous polyethersulphone (PES) membranes (Alvarez *et al.*, 2004). The Chemcatcher also uses a PES membrane but the receiving phase of the sampler is a solid-phase extraction (SPE) Empore disk (Kingston *et al.*, 2000). In some cases this device has been used with the disk directly exposed to the water (i.e. without a membrane) (Shaw and Muller, 2005; Gunold *et al.*,

2008; Shaw *et al.*, 2009). The principle of contaminant accumulation in these samplers is based on the diffusion (as a result of the concentration gradient between the water and the sampler's receiving phase initially free of the chemical of interest) of the chemicals through a diffusive boundary layer at the surface the sampler, transport through the PES membrane (with possible interaction with the membrane material) and adsorption to the sorbent phase. Single-phase polymeric devices such as silicone or polyoxymethylene (POM) have also been used for the sampling of certain polar substances, however the concentration in the sampler reaches equilibrium with that in the water rapidly, precluding them from being used for integrative sampling. It is clear that not a single device configuration will cover all substances of interest.

One added challenge with integrative samplers for polar substances is the complex sorbate-sorbent interactions that take place during the contaminant adsorption to SPE sorbents such as OASIS HLB (Bauerlein *et al.*, 2012). These researchers showed that solute-sorbent interactions for certain polar substances could be best modelled by a double Langmuir model showing the presence of multiple binding sites on this sorbent. *In situ* calibration of the POCIS sampler in wastewaters by Harman *et al.* (2011a) showed possible solute competition for sorption sites on the HLB sorbent or rapid equilibrium for substances such as metoprolol acid (a beta blocker) and for OH-cotinine (a nicotine metabolite).

Time-weighted average concentrations can be calculated if the sampling rate, R_s is known. Different procedures as reviewed by (Harman *et al.*, 2012) have been used over the last decade for the estimation of sampling rates. The most simple systems are static renewal (small volume exposures with periodically renewed exposure solution) and static depletion (small volume exposures with no renewal and first order model fitted to water concentration changes). The latter results in possible positive control issues and does not allow to properly vary water turbulences to assess the effect of water turbulences on R_s . Flow-through calibration systems (large volume constant flow of fortified exposure solution) are more resource intensive but do not suffer from positive control issues. Another possibility is to perform calibrations *in situ*. Calibrations are performed at the measurement site. While this procedure is resources intensive, it is also likely to provide the most accurate sampling rates if ambient dissolved water concentrations can be measured accurately. A literature review of POCIS sampling rates showed that R_s are generally in the range of a few ml per day up to 2.5 L d⁻¹ depending on the compound, exposure conditions and the calibration set-up. Sampling rates measured so far tend to be around or below 0.5 L d⁻¹. Out of all factors that can affect sampling rates (temperature, fouling, pH, salinity or DOM), water turbulences appeared to have the most pronounced effect on sampling rates (Harman *et al.*, 2012). It is generally difficult to apply sampling rates obtained in the laboratory to *in situ* deployments where exposure conditions may be different to those used during calibration experiments. The use of the PRC approach widely applied to samplers for nonpolar substances is much more challenging for polar samplers such as the Chemcatcher or POCIS devices (Harman *et al.*, 2011b). The PRC approach requires isotropic exchange between water and the sampler which is challenging for adsorption-based samplers.

The understanding of the processes that control POCIS sampling rate for various classes of chemicals remains limited. The often-seen wide differences in sampling rates obtained in calibration experiments under quiescent and turbulent conditions tend to show that the thickness of the water boundary layer often plays an important role. As shown by the *in situ* calibration and modelling work by Vermeirssen *et al.* (2012), the PES membrane may affect the R_s for analytes that sorb significantly to it

($\log K_{ow} > 2$) and can be responsible for the lag-phase observed during the initial sampling phase. When a lag phase is present, linear accumulation can be observed once the concentration on the PES membrane has reached equilibrium with the water. The occurrence of a lag phase may have implications for the accuracy of the measurement but also indicates that the membrane pore size may also influence the sampling. Recent work by Fauvelle *et al.* (2012) showed that for some chemicals changing the sorbent phase inside the POCIS device (OASIS HLB by OASIS MAX) caused not only a change in half-life (time to 50 % of an apparent equilibrium), but also a change in R_s . This implies that processes occurring in the receiving phase influence to some extent the sampling rate.

As a result of the unavailability of an exposure-correction method, recent developments have focussed on applying the Diffusion Gradient in Thin film Technique (DGT), until now applied to trace metals (Davison and Zhang, 1994) to the monitoring of pharmaceuticals such as antibiotic (Chen *et al.*, 2012). A polyacrylamide or agarose gel layer of known thickness is combined with a sorbent such as XAD-18 to produce a passive sampling device whose sampling rates are relatively independent of water turbulences around the sampler. Recent studies have involved the measurement of sampling rates and diffusion coefficients for antibiotics through the gel layer (Chen *et al.*, 2012). A drastic reduction in sampling rates was observed as a result of the smaller sampling window of the DGT device (3.14 cm²) compared with that of the POCIS and the use of the diffusion-limiting gel. This reduction in mass accumulated is compensated to an extent by the cleaner extract obtained with the gel (less impact of ion suppression with LC-MS for example). Biofouling, the need for a PES membrane to protect the hydrogel layer and very stagnant water conditions may remain an issue. A recent study involving a DGT configuration but with the OASIS HLB demonstrated a linear uptake for compounds such as the acidic herbicide 2,4-D (Fauvelle, unpublished data) over 20 days compared with a curvilinear accumulation seen with the standard POCIS version.

Conclusions to Ian Allan's presentation were that, so far, many calibration studies for devices such as the POCIS or Chemcatcher have been performed. However, a limited number of these studies actually aimed at understanding processes and mechanisms involved the accumulation of different substances and classes of chemicals (which processes control the uptake and dictate what the sampling rate will be). Since an exposure-correction method is still lacking for samplers such as the POCIS, will semi-quantitative data be sufficient? Links between sampling rates and compound properties are still lacking. Further work should perhaps aim to measure sorption isotherms for various sorbents, evaluate the impact of interactions with the membrane on the sampling rates and further develop techniques such as DGT involving diffusion-controlling barriers with sampling rates independent of water turbulences.

5.2 Discussion on passive sampling of marine and transitional waters

A distinction has to be made between passive sampling methods for metals, volatile organic compounds, non-volatile/semivolatile nonpolar organic compounds, and polar organic compounds. A further distinction should be made with respect to the degree of sampler-water equilibrium that can be established. For the analysis of volatile organic compounds (e.g., benzene, dichloromethane), solid phase microextraction (SPME), usually carried out as a headspace analysis method, has a long standing record (Zhang and Pawliszyn, 1993; Ji *et al.*, 2006; Tang and Isacson, 2008). This method is typically applied for field water samples that are brought to the laboratory, rather than as an *in situ* passive sampling method. Volatile organic compounds were

not considered further by WKPSPD. Passive sampling of metals was not further evaluated either, as explained in Section 4.

Kinetic sampling and equilibrium sampling. An appreciation of the difference between kinetic sampling and equilibrium sampling is vital for a proper understanding of the information that PSD can and cannot provide. During the initial sampling stage, PSDs can be regarded as an infinite sink, and accumulated amounts reflect the time weighted average concentrations during the deployment. During prolonged deployment, the contaminants gradually attain their equilibrium concentrations. The time scale for equilibrium attainment (τ) depends on the sampling rate (R_s) and on the product of sampler mass (m) and sampler-water partition coefficient (K_{sw}), such that $\tau = K_{sw} m / R_s$. The sampling rate in turn is determined by the overall mass transfer coefficient (k_o) and the sampler surface area (A), viz. $R_s = k_o A$, hence $\tau = K_{sw} m / (k_o A)$ (Huckins *et al.*, 2006; Booij *et al.*, 2007). Mass transfer of metals (DGT sampler) and of compounds with $\log K_{ow}$ values < 3-5 (nonpolar samplers) is typically controlled by transport within the membrane, and sampling of hydrophobic compounds by nonpolar samplers is typically controlled by the water flow rate and particle density near the sampler surface. Equilibration times can be manipulated to some extent by changing the mass/area ratio of the sampler (m/A), the water flow rate or membrane thickness (k_o), and the choice of a sampling material for which the target analyte has a higher or lower affinity (K_{sw}). The accuracy of C_{free} values is primarily determined by the accuracy of K_{sw} for compounds that reach equilibrium during the exposure, and by the accuracy of R_s for those compounds that remain in the kinetic stage of the sampling process.

The idea of using a passive sampling matrix as a reference phase for organic compounds was much discussed. The idea behind the reference phase concept is that toxicity data and monitoring data could be expressed in terms of the compound's equilibrium concentration in a commonly accepted reference polymer (Mayer *et al.*, 2003). This approach was considered to be scientifically sound. It was also acknowledged that the use of a reference phase makes the accuracy of sampler-water partition coefficients less critical because concentrations in the PSDs are used as such in this case, without the need to calculate C_{free} . Practical difficulties are that the scientific community should agree on a universal reference phase for which all target analytes reach equilibrium within a reasonable timeframe, at least partially. The condition of rapid equilibrium attainment is fulfilled for passive sampling with PDMS in sediments and in lipid extracts (see Sections 6 and 7), but generally not for passive sampling in the water column, where equilibrium attainment for compounds with $\log K_{ow}$ values > 5.5 is rarely observed.

Sampler-water partition coefficients. The availability of accurate K_{sw} values was identified as a key issue for compounds that reach complete or partial sampler-water equilibrium. With kinetic sampling, the sampling rate (R_s) is the critical factor. The R_s can be either controlled by exposing the PSDs under a forced flow regime (Chen and Pawliszyn, 2004; Ouyang and Pawliszyn, 2007; Llorca *et al.*, 2009) or by increasing the mass transfer resistance of the membrane to such an extent that it is much higher than the mass transfer resistance of the water boundary layer. The latter approach was chosen for metal sampling by DGT (Davison and Zhang, 1994) and by organic contaminant sampling by MESCO (Wennrich *et al.*, 2003) and ceramic dosimeters (Martin *et al.*, 2003). The use of a large membrane resistance inevitably reduces the sampling rate and increases the detection limits. In cases where R_s cannot be controlled from the sampler design (flow control or membrane resistance), it must be calculated from the dissipation of performance reference compounds (PRCs)

(Huckins *et al.*, 2002). The PRC method in turn requires accurate knowledge of the K_{sw} values of these PRCs (Booij and Smedes, 2010), but the accuracy of K_{sw} values of target analytes that remain under kinetic sampling is of secondary importance. A special case of the PRC method stems from the SPME literature, where the degree of equilibrium for target analytes is inferred from the fractional dissipation of isotopically labelled analogues (Chen and Pawliszyn, 2004). The latter method requires that at least partial equilibrium is attained.

The experimental determination of K_{sw} values of nonpolar contaminants is not an easy task, as evidenced by the high interlaboratory variability of 0.2 to 0.5 log units (Difilippo and Eganhouse, 2010; Lohmann, 2012; Lohmann *et al.*, 2012). A similar high variability is observed from the literature on octanol-water partition coefficients and the same may hold for bioaccumulation factors and sediment-water partition coefficients. WKPSPD considered that the uncertainty of K_{sw} should be inferred from interlaboratory variability, that guidelines for the determination of these values should be developed to reduce this variability, and that K_{sw} values only be accepted if interlaboratory variability is below a defined threshold.

WKPSPD considered that the experimental determination of sampler-sampler partition coefficients is less difficult than the measurement of sampler-water partition coefficients, and that the definition of a primary polymer standard is worth considering.

Are we to use the same sampler everywhere? This question was discussed in Section 4.2 above (subsection “Standardization”).

Polar contaminant sampling. The evidence presented by Ian Allan on the state of the art of polar passive samplers (Section 5.1.3) indicates that these devices presently are not mature enough for quantitative assessment of the levels of polar contaminants, although they can be very useful for semi-quantitative assessments, as required in investigative monitoring. Research challenges for polar samplers are to elucidate the factors that determine the magnitude of the sampler-water sorption coefficients, and the factors that control the sampling rates.

Uncertainties. The QA/QC Directive requires a combined uncertainty of <50% at the EQS concentration. Whilst a 50% uncertainty target would be achievable for the determination of analyte concentrations in the passive sampler, it is difficult to attain for passive sampling based C_{free} , due to there being additional error sources (e.g. mainly on the K_{sw} values of the analytes and the PRCs). Because sampling rates of hydrophobic compounds weakly decrease with molecular size (Booij *et al.*, 2003b; Huckins *et al.*, 2006; Booij and Smedes, 2010; Rusina *et al.*, 2010), it is expected that the uncertainties in the use of different models are minor. Although an uncertainty target for C_{free} would be larger than currently permitted for C_w , it should be borne in mind that measurements of C_{free} include aspects of sampling uncertainty which are currently excluded. Overall, there is a need to focus on and improve each of the individual uncertainties, particularly those around the partition coefficients, as well as the sampling rate calculations carried out afterwards.

6 Session 3: Passive sampling of sediments

6.1 Presentations

6.1.1 Philipp Mayer, Kimmo Mäenpää, Annika Jahnke & Gesine Witt: "Equilibrium sampling of hydrophobic organic pollutants in sediment."

For hydrophobic organic contaminants chemicals (HOCs), passive sampling of sediments has several practical and conceptual benefits compared to passive sampling of water. Concentrations of HOCs in sediment are much higher and generally also more stable than in water, which allows relatively small sediment samples (e.g. 100-500 grams) to be brought to the laboratory and the equilibrium sampling to be conducted under controlled and agitated conditions. This speeds up the sampling kinetics, and significantly extends the applicability domain of equilibrium sampling into the high Log K_{ow} range of pollutants, which hardly can be equilibrated within the water column. Equilibrium sampling of sediment can provide precise measurements of freely dissolved concentrations in sediment, which express chemical activities that drive benthic bioaccumulation and various partitioning processes of the pollutants.

Sampling should be conducted at equilibrium and without depletion of the sediment phase. The fulfilment of both criteria can be confirmed by parallel sampling with varying coating thicknesses, which is easily achieved *ex situ*, for example by rolling the sediment sample in bottles coated with different thicknesses of PS polymer (Maenpaa *et al.*, 2011). This was demonstrated for samples taken along a pollution gradient within the Stockholm archipelago. Glass jars with micrometer thin PDMS coatings of three thicknesses were used for the sampling, which allowed equilibrium sampling of the full PCB range within 2 weeks. The method was rather sensitive with LoQ of 16-800 fg/L for ICES7 CBs (GC-HRMS) and very precise with relative standard errors generally well below 10%. This study showed that sediments were a diffusive source of PCBs and that Stockholm is a source of PCBs to the Baltic Sea. *Ex situ* PS of sediments is able to achieve equilibrium to a higher log K_{ow} than *in situ* water sampling is able to achieve, which means that PS of sediments facilitates the interpretation of toxicity data from passive dosing bioassays. *In situ* PS of sediments has also been demonstrated successfully by inserting SPME fibres held within a copper housing in to the sediment using divers to deploy and retrieve the samplers (Witt *et al.*, 2013).

6.1.2 Foppe Smedes: "Compounds in silicone rubber passive samplers equilibrated with marine sediments."

Passive sampling of sediment is generally performed on samples brought to the laboratory. A portion of sediment is suspended in a small amount of water and is exposed to a passive sampler until equilibrium is obtained. Freely dissolved concentrations in the pore water (C_{free}) can be estimated through dividing the concentration in the sampler (C_p) by the passive sampler partition coefficient (K_{pw}). In comparison to passive sampling in surface water, the uptake of compounds by these samplers (e.g., 0.5 mm thick) from sediment is much faster, and equilibrium can be obtained in 28 days for e.g. dibenz[*a,h*]anthracene. However this uptake may "dilute" or deplete the system so the result may not reflect the situation present before the passive sampler was introduced. This depletion can also be forced by increasing the size of the sampler in parallel with decreasing the amount of sediment. Increasing sampler/sediment ratios result in lower concentrations in the pore water and in the sediment. This multi ratio method allows to construct a desorption isotherm of which both the original C_{free} (low sampler/sediment ratios) as well as a measure for

the accessible or releasable concentration (high sampler/sediment ratios) can be calculated (Smedes *et al.*, 2013a). This research further showed that uptake was faster when the suspension contents were highest, likely because this will also cause the highest particle content in the water boundary layer decreasing the diffusion distance between sediment and sampler. Non-depletive incubations (low sampler/sediment ratios) resulted in the longest time to reach equilibrium and the highest concentration in the sampler. Consequently, the largest uptake per unit of surface area is needed. Obviously, for a thinner film the necessary uptake per unit of surface area is much smaller and equilibrium is attained much faster.

Thin silicone films coated on the inside of glass bottles were used by the National Institute of Coastal and Marine Management (RIKZ) in the Netherlands in several Projects and case studies (MODELKEY) and also in the ICES Passive sampling Trial Survey and Intercalibration (Smedes *et al.*, 2007c). In this study, centrally prepared silicone rubber coated bottles were distributed over 13 laboratories and one or two local sediments were exposed in duplicate. After equilibrium one bottle was analysed by the participating laboratory and the other sent to the central laboratory that analysed one replicate sample of all the exposures from participants for reference. The results of these samplers allowed an excellent European wide spatial comparison of C_{free} in sediment pore water for PCBs and PAHs, showing clearly where the hotspots were situated. Because additionally passive samplers were also deployed in the overlaying water, the relationships between concentrations in the sediment pore water and the surface water could be investigated. This showed good agreement for shallow waters (as expected) and an obvious disagreement in a 400 m deep fjord. This disagreement was for the local pollution of bottom sediment with PAHs but not for compounds like PCBs and HCB that are present at that location because of diffusive pollution.

A further example showing the power of passive sampling is a study within the ICON project. Silicone rubber samplers were exposed to sediments from Iceland to the Mediterranean including several offshore stations. Samplers concentrated a large variety of compounds which were detectable in basically all samples. These were PCBs, PAHs, musks, organophosphorus compounds, p,p'-DDE, PBDEs, chlordanes among others. Surprising was that also some very water soluble organophosphorus compounds were found in the sediments. Classical sediment analyses only showed the presence of some PAHs and occasionally some PCBs.

The studies support the conclusion of the WGMS in 2007 that passive sampling of sediments is an easily applicable technique that requires little effort for implementation. Results of traditional sediment monitoring only show a limited relationship between concentrations in sediments and concentrations in overlaying water and biota, even when appropriate effort has been made by sieving the sediments. The C_{free} measured in the pore water by PS is a direct measure for the impact that a sediment can have on the overlaying water, as contaminant source or sink. This is all done on the raw sediment and results do not require any normalization.

The presentation was concluded by giving practical considerations and suggestions for QA on the process of passive sampling applied in sediments for spatial and temporal trend monitoring. When appropriate BAC and EAC are available, PS of sediments can also be used for environmental assessment purposes.

6.1.3 Philipp Mayer: "Conclusions from the Pellston workshop on bioavailability/bioaccessibility measurements using passive sampling devices for the management of contaminated sediments."

A summary of the SETAC Technical Workshop "Guidance on Passive Sampling Methods to Improve Management of Contaminated Sediments" was presented. The Executive Summary from this meeting is available from the internet (Parkerton *et al.*, 2013). The Pellston workshop concluded that PS-based measurements of C_{free} provide a better basis for assessing and predicting toxicity and bioaccumulation by benthic organisms compared to using total sediment concentrations in combination with normalization procedures and the application of generic K_d values. Passive sampling was found to have the potential for significantly improving the risk assessment of contaminated sediments in general, and for characterising the exposure of benthic organisms, fluxes to the overlying water column and exposures within the water column in particular.

The SETAC workshop recognised that passive metal sampling in sediments is largely a future opportunity, whereas sampling of nonpolar organics was considered to be well established. Issues to be addressed in the future for passive sampling of nonpolar contaminants are that consensus be reached on guidance for measuring K_{sw} , for assessing the degree of sampler-sediment equilibrium, and for assessing non-depletion of the sediment phase during the PSD exposure.

6.2 Discussion on passive sampling of sediments

Rationale of PS in sediments. Concentrations of dissolved contaminants in pore waters are a better proxy for toxicity of benthic organisms than total concentrations of metals and nonpolar organic contaminants in the sediments (Di Toro *et al.*, 1991). This is not to claim that uptake via the water phase is the only exposure route, but rather that uptake via direct contact or ingestion of particles does not result in a significant increase in body burden higher than the equilibrium level. (Burgess *et al.*, 2013). Because of the difficulties of analysing pore waters, alternative assessment schemes have been developed that relate concentrations in pore waters to those in the sediment, taking into account the interactions between the contaminant and specific phases, such as acid volatile sulphides, amorphous organic carbon, and black carbon (Burgess *et al.*, 2013). For example, it has been observed that the affinity of PAHs for black carbon is 1.5 to 3 orders of magnitude higher than their affinity for amorphous organic carbon (Gustafsson *et al.*, 1997). Jonker and Koelmans (2002), observed that the black carbon to water partition coefficients of PAHs and PCBs strongly depend on the nature of the sorbent, which further complicates the calculation of C_{free} from the concentrations in the sediment. The number of sediment characteristics that can be taken into account for deriving a best estimate of concentrations in the pore water is countless, and a balance must be found between practical applicability and appropriateness.

Mobility and chemical activity. Passive sampling can be used in two different ways for the risk assessment of contaminated sediments: (1) as a depletive method for measuring the (readily) desorbing contaminant fraction of the sediment, and (2) as a negligible-depletive method for measuring freely dissolved concentrations in the sediment pore water (Cui *et al.*, 2013). (1) Depletive sampling of sediment slurries with poly(2,6-diphenyl-p-phenylene oxide) (Tenax) has been used to separate contaminant fractions that show rapid, slow, and very slow desorption rates (Cornelissen *et al.*, 1997a; ten Hulscher *et al.*, 1999). It has been suggested that the high K_{oc} values can be quantitatively explained by the size of the (very) slowly desorbing contami-

nants (Cornelissen *et al.*, 1997b; ten Hulscher *et al.*, 1999). (2) Passive sampling that is operated in the negligible depletion mode can be used for measuring freely dissolved concentrations in sediment porewater. In this case, care should be taken that contaminant uptake by the sampler does not cause significant depletion of the mobile contaminant pool in the sediment phase (Mayer *et al.*, 2000).

The presence of particles near the sampler surface results in much higher sampling kinetics compared with PS in the water column (Booij *et al.*, 2003a; Mayer *et al.*, 2005; Mayer *et al.*, 2007; Smedes *et al.*, 2013a). This allows samplers to reach equilibrium for nonpolar compounds with $\log K_{ow}$ values up to around 7 within a few days/weeks, when incubated in agitated sediment suspensions. For passive sampler exposures to stagnant sediments the equilibration times are much higher (Mayer *et al.*, 2000; Booij *et al.*, 2003a; Maruya *et al.*, 2009). For nonpolar compounds the transport models to estimate C_{free} for kinetic sampling in static sediments are rather complex (Booij *et al.*, 2003a; Fernandez *et al.*, 2009a; Fernandez *et al.*, 2009b) and not advisable for routine application. So far there is no reason to assume that *in situ* methods have an advantage over laboratory based passive sampling methods for nonpolar compounds, but this may be different for passive metal sampling. SPME has proven to be an excellent method for determining chemical activities of nonpolar compounds in undisturbed sediments at high vertical resolution (Maruya *et al.*, 2009; Witt *et al.*, 2009). Smedes *et al.* (2013a) developed a method to measure the concentrations of mobile nonpolar contaminants in the sediment phase and C_{free} in the pore water, by incubating sediments and silicone sheets at increasing polymer/sediment mass ratios. At low ratios, this method yields C_{free} (without depletion of the sediment phase). At high ratios the accessible contaminant pool in the sediment phase can be assessed (maximal depletion).

The evidence that contaminant toxicity and body burden for benthic organisms is directly linked to concentrations in SPME fibres at equilibrium and to the rapidly desorbing fraction as determined with the Tenax extraction method was recently summarised by You *et al.* (2011). These authors conclude that a single point Tenax method is more labour effective, and has lower detection limits, and that SPME can be applied to a wider range of compounds. They call for the further development of kinetic sampling methods to overcome the need for excessive exposure times for equilibrium sampling of very hydrophobic compounds. Harwood *et al.* (2013) observed that the Tenax and the SPME method performed equally well in explaining bifenthrin toxicity to a chironomid and crustacean for three sediments that spanned a 5 fold difference in organic carbon content.

The SETAC technical workshop on “Passive Sampling Methods to Improve Management of Contaminated Sediments” concluded that passive sampling in sediments was well established for nonpolar organic compounds, whereas passive metal sampling in sediments was considered to be largely a future opportunity (Parkerton *et al.*, 2013). Issues to be resolved are the accuracy of K_{sw} and the assessment of equilibrium attainment at the end of the sediment-sampler exposure. WKPSPD agreed with these conclusions.

Equilibrium assessment and (non)depletion. In order to assure that valid measurements are made, passive sampler exposures in sediments should be properly scaled. If the aim of a study is to determine the C_{free} in the pore water, then the sediment phase should not be significantly depleted due to contaminant uptake by the sampler. This condition is fulfilled when the sorption capacity of the sampler (sampler mass times sampler-water partition coefficient) is much smaller than the sorption

capacity of the sediment (organic carbon mass times K_{oc}) (Mayer *et al.*, 2000; Booij *et al.*, 2003a). For the case of kinetic sampling, the sampling rate should be smaller than the desorption rate from the sediment (Booij *et al.*, 2003a). If the aim is to determine the mobile contaminant fraction in the sediment phase, then the sorption capacity of the sampler should be much higher than that of the sediment, and an increase in sampler mass should not result in a higher contaminant amount in the sampler phase. The establishment of equilibrium can be verified if the sampled amounts are linearly proportional to the sampler thickness (keeping the sampler surface area constant) (Reichenberg *et al.*, 2008; Maruya *et al.*, 2009; Maenpaa *et al.*, 2011). The use of performance reference compounds also assists in the evaluation of non-depletion and equilibrium attainment. If the PRCs are quantitatively dissipated from the sampler, then this indicates that equilibrium has been attained for compounds with hydrophobicities up to that of the most hydrophobic PRC. However, the reverse is not necessarily true: a partial dissipation of PRCs may either indicate that equilibrium has not been attained, or that the sorption capacity of the sampler is not negligible compared with that of the sediment (i.e., partial dissipation of PRCs may also be indicative of depletion of the sediment phase).

There was a consensus within WKPSPD that equilibrium passive sampling in sediments is preferable over kinetic sampling because of its conceptual and mathematical simplicity. When equilibrium cannot be attained on practical time scales, kinetic sampling is an acceptable alternative that is not more complicated than passive water sampling. WKPSPD also highlighted the low detection limits that could be achieved with the passive sampling of hydrophobic compounds in sediments.

7 Session 4: Linking passive sampling to concentrations in biota

7.1 Presentations

7.1.1 Foppe Smedes: "Surface water passive sampling and concentrations in biota."

The presentation started with the statement that passive sampling cannot predict concentration in organisms. Organisms function differently under varying environmental conditions. Concentrations vary between species and often depend on parameters like age, sex, size and many other factors. As an example lipid based concentrations of PCB153 in a number of different species at two stations in the Western Scheldt were compared. These were showing a large variation over species, but for the individual species the concentration ratio between the stations was about equal. This ratio also matched the ratio between the results from passive sampling at these two stations. This example showed that passive sampling senses the differences in space in an equal way as organisms do. The ICES Passive Sampling Trial Survey (PSTS) showed a clear relationship between concentrations in organisms and passive sampling results. Concentrations of PCBs and PAHs in mussels correlated very well with the freely dissolved concentrations obtained by passive sampling. Bioaccumulation factors calculated from these data were highly correlated to the K_{ow} . This was the case for areas with low concentrations as well as for more polluted areas.

Also data from a monitoring program in the Netherlands, running for over ten years now, that used silicone rubber passive samplers in parallel with deployed mussels (*Mytilus edulis*) showed clear relationships between freely dissolved concentrations and concentrations in mussels. Two significant outliers were noticeable, PCB 170 and 180, that had about a factor three to four lower accumulation in mussels than expected. Remarkably, PCB 187 was behaving as expected.

Using passive sampling results to calculate Bioaccumulation Factor (BAF) values of several freshwater organisms (eel, zebra mussel, roach) for PCBs, PAHs, HCB, p,p'-DDE and some BDEs revealed a general trend that BAF were close to the K_{ow} , indicating that no clear biomagnification was observed.

In traditional biomonitoring whole organisms or tissues are analysed (route 1 in Figure 1) and results compared to EQS values in spite of the variability connected to the monitoring of organisms. Alternatively concentrations in organisms could be predicted from passive sampling results using BCF or BAF values (route 3 in Figure 1). However, literature data for BCF/BAF values typically cover a rather large range due to variations in measurement conditions and the variability between organisms. A further alternative is to recalculate EQS values to freely dissolved concentrations (C_{free}) for a direct comparison with PS results. Another alternative is to directly transfer the concentration taken up by the sampler to a lipid based concentration (route 4 in Figure 1) through known distribution of compounds between a model lipid (e.g., triolein) and the polymer used. In this way a kind of abiotic lipid based concentration is obtained that represents a level that would be found in an organism if it was in equilibrium with the surrounding water. In this approach all factors that cause variable concentrations in biota like species biomagnification, regulation, metabolism or biodegradation do not contribute to the variability.

Figure 2 shows the relation of such an abiotic lipid based concentration plotted versus the one measured in deployed mussels for the 8 stations in the above described

monitoring program in the Netherlands. Autumn and winter samplings were plotted separately. The error bars indicate the temporal variability of both mussel and abiotic concentrations over the period of 2006–2010. The slope of 0.3 means that lipid based concentrations in the mussels are 30% of the predicted model lipid based concentration. This is quite acceptable, considering that mussel lipids are very different from the model lipid. Both freely dissolved and abiotic lipid based concentrations derived from passive sampling are valid alternatives to classical biomonitoring but with a number of advantages (Table at the bottom of Figure 1), including worldwide comparability.

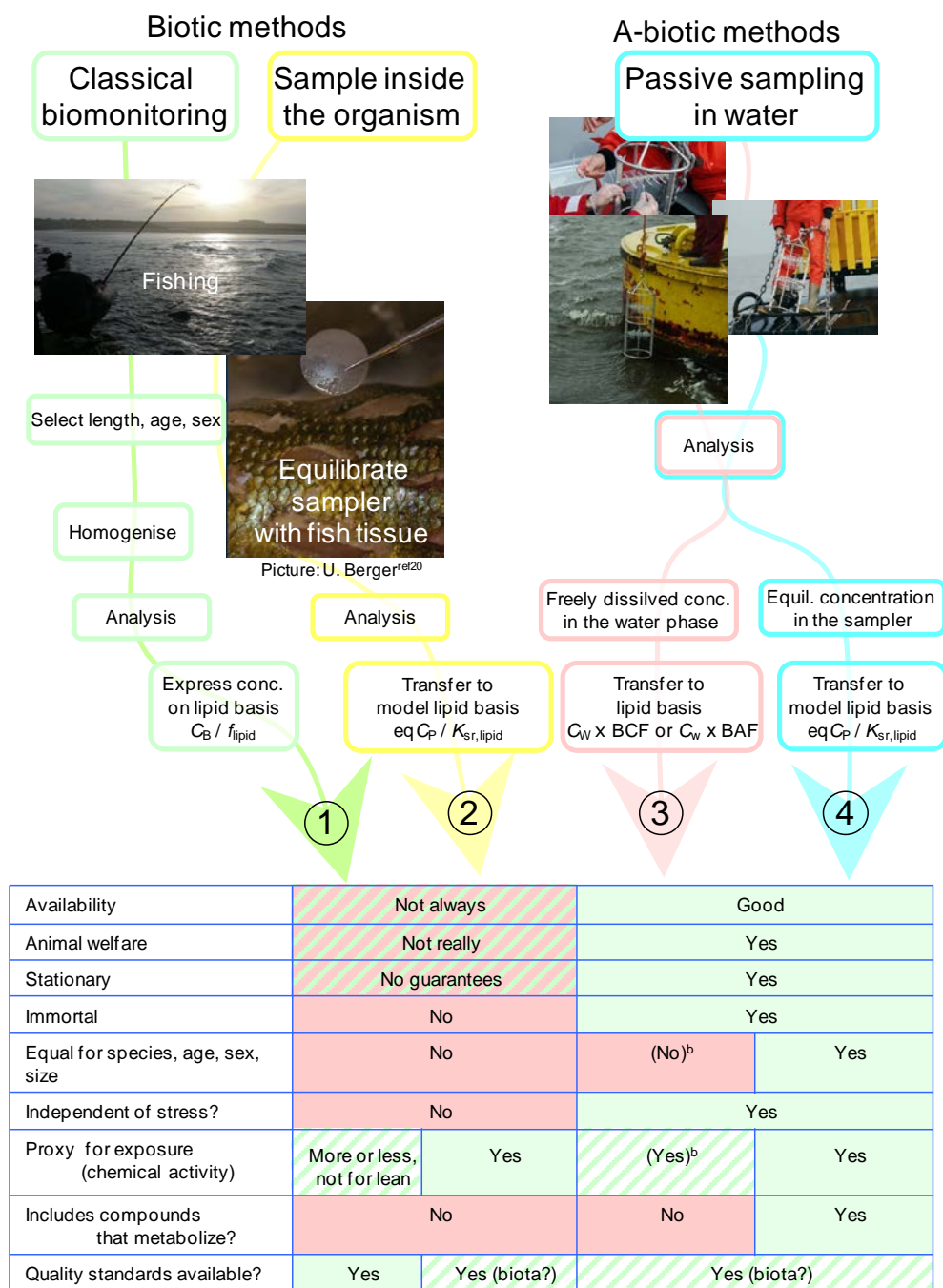


Figure 1. The biotic and abiotic routes to lipid based concentrations.

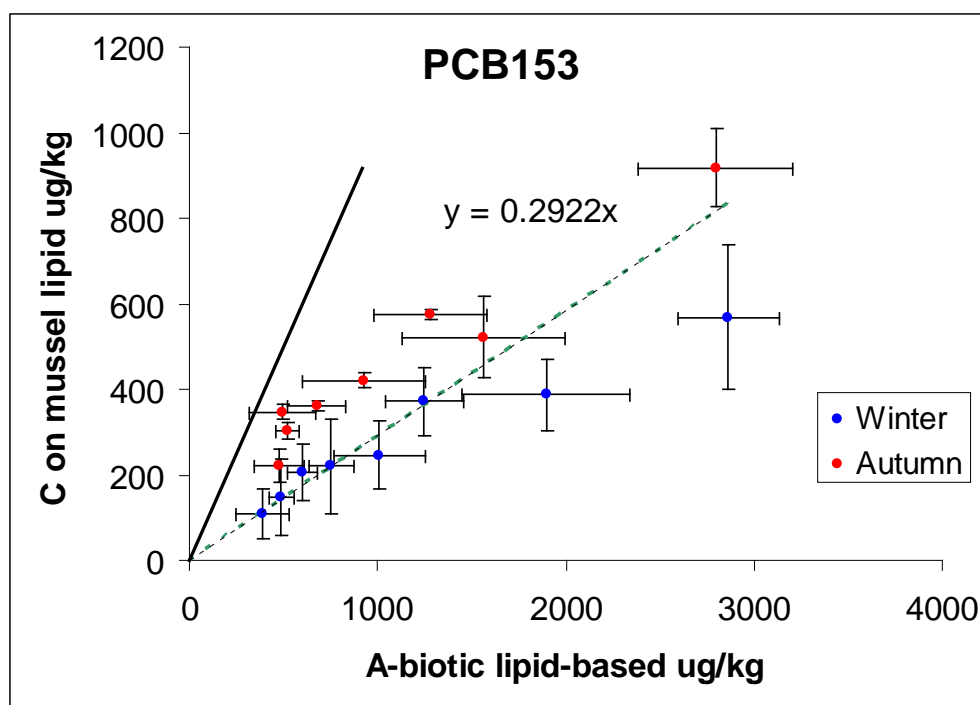


Figure 2. PCB153 in mussel lipid and abiotic lipid for 8 monitoring stations in the Dutch coastal waters (period 2006–2010). Bars indicate the temporal variability. (Smedes *et al.*, 2013b).

7.1.2 Philipp Mayer, Stine N. Schmidt, Annika Jahnke, Kimmo Mäenpää: “Calibrating passive sampling and passive dosing techniques to lipid based concentrations.”

This presentation gave four reasons why calibrating passive sampling measurements to lipid based concentrations is useful for hydrophobic organic chemicals:

- In environmental monitoring: to link passive sampling measurements directly to lipid normalised biota concentrations
- For studying/predicting bioavailability/bioconcentration from sediment/soil
- For *in situ* tissue sampling and comparison with biota concentrations
- In PS/PD for linking effects to internal or target site exposure

Bioconcentration can often be well predicted from passive sampling measurements: the concentration in the polymer is measured and translated to C_{free} using a polymer to water partition coefficient ($C_{\text{free}} = C_{\text{polymer}} / K_{\text{polymer,water}}$), and this C_{free} is then multiplied with a BCF value ($C_{\text{biota}} = C_{\text{free}} \cdot \text{BCF}$) (Kraaij *et al.*, 2003). While this approach has been successfully applied in many studies, it still has the weakness that the division with K_{polymer} and subsequent multiplication with BCF can introduce significant numerical error, particularly when these factors are very high. Recently, a more direct approach was proposed, where the water phase is omitted and the translation from polymer to lipid is done in one step. In this approach, the equilibrium partition concentration in lipid ($C_{\text{lipid,partition}}$) is determined as the product of measured concentration in the polymer and a lipid to polymer partition coefficient ($K_{\text{lipid,polymer}}$). The obtained equilibrium partition concentrations in lipids can then either be used for predicting biota levels under an equilibrium assumption, or they can be used as a thermodynamic reference for assessing actually measured concentrations in biota. The utility of this approach was demonstrated using examples from published literature (Jahnke *et al.*,

2008; Mayer *et al.*, 2009; Maenpaa *et al.*, 2011). SPME fibres equilibrated over samples or calibrated over spiked olive oil, compared with PDMS coated vials of different thicknesses gave comparable results. Calculated $C_{\text{lipid,partitioning}}$ values were comparable but somewhat higher than actually measured lipid normalised concentrations in chironomids.

Passive dosing (using PDMS) of springtails demonstrated that the toxicity of a mixture of PAHs was directly related to the sum of the chemical activities and to the sum of PAH $C_{\text{lipid by partitioning}}$.

7.2 Discussion on linking passive sampling to concentrations in biota

Chemical monitoring using biota is presently done to assess contaminant chemical activity in the water phase, to determine spatial and temporal trends, and to evaluate the risk of secondary poisoning of predators. The ability of PS to complement or replace biomonitoring for either purpose is discussed below. In addition, the recent application of PS in biota homogenates and extracted lipids will be highlighted.

Chemical activity proxies. It is widely recognised that concentrations of dissolved contaminants are a valuable proxy for chemical activity, or contamination pressure, because knowledge of these concentrations allows to estimate the equilibrium concentrations in other environmental compartments (sediments, air, biota) from the respective partition coefficients (section 5) (Di Toro *et al.*, 1991; Arnot and Gobas, 2003; EU, 2011; Lohmann *et al.*, 2012; Burgess *et al.*, 2013). The low concentrations that are found in the water phase make a high sample intake necessary when batch sampling is used. This could be laborious and costly, and carries a high risk of sample contamination. With passive sampling, detection limits in the low pg L^{-1} are achievable without much difficulty (Mills *et al.*, 2011). Biomonitoring can in principle be used as an alternative to water monitoring, provided that the bioaccumulation factors (BAF) are accurately known and that contaminant concentrations in the monitored species are at their equilibrium or steady-state values. Reported BAF values show a high variability among studies, even for the same species. For example BAF values for the blue mussel varied by several orders of magnitude among eight studies (Booij *et al.*, 2006). Arnot and Gobas (2006) reviewed >7000 BCF and BAF values and concluded that 45% of the data suffered from one or more major source of uncertainty. Field based BAF of HCB in the River Elbe spanned a factor of 18 and 17 for bream and eel, respectively (EU, 2005). Considering this high BAF variability, concentrations in biota are not a very good proxy for chemical activity, and passive sampling should be used for this purpose instead.

Spatial and temporal trends. Biomonitoring has extensively been used to assess spatial and temporal trends of contamination by nonpolar contaminants and trace metals (Goldberg, 1975; Lauenstein, 1995; Lauenstein and Cantillo, 2002; Monirith *et al.*, 2003). The limitations of using sentinel organisms for comparing contamination levels in time and space are generally recognised. The physiological state of the organism may vary over space and time, multiple species may be needed for obtaining a good geographical coverage (e.g., oysters, blue mussels, green mussels, zebra mussels) and sometimes may not be available (e.g., off-shore environments, deep sea, anoxic or toxic locations). These issues do not exist for passive samplers when results are expressed as C_{free} (rather than as an accumulated amount per unit sampler mass), but WKPSPD recognises the value of historical data obtained for biomonitoring organisms, and discussed how existing data can be linked to future passive sampling data. Booij *et al.* (2006) evaluated the results of nine mussel-SPMD comparison studies, and concluded that BAF values were the major source of variability in the

SPMD/mussel concentration ratios, and that site-specific repetitive parallel exposures are needed to convert historical biomonitoring data to current passive sampling data. Smedes (2007) observed for PAHs and PCBs a close correspondence between passive sampler based C_{free} and concentrations in mussels, over four years, two sampling seasons, and eight estuarine and coastal monitoring stations. Standard deviations of the observed concentration ratios ($n=60$) were about 0.15 log units for PCBs and about 0.20 log units for PAHs. Average $\log BAF$ values were highly correlated ($R^2=0.94$) with $\log K_{ow}$ (range 4.5 to 7). These results indicate that the transition of biomonitoring time series to a passive sampler based time series is feasible with modest effort.

Predator diet. Under the WFD, EQS values in biota are defined for hydrophobic and other substances (e.g. Hg) where secondary poisoning is a significant hazard pathway (EU, 2011). In the most current revision of the EQS Directive “biota” is defined as whole fish for most substances, exceptions are for PAHs (crustacea and molluscs), and for dioxins, PCBs, and similar compounds (fish, crustacea and molluscs) (EU, 2013). Passive samplers can be used to accurately predict concentrations of PAHs and PCBs in mussels (Smedes, 2007) and may be a suitable alternative to monitoring in molluscs for these compounds. However, the WFD requires other substances, including Hg, PBDEs, dicofol, PFOS, HBCDD and heptachlor/heptachlor epoxide, to be monitored in whole fish for comparison against biota EQS values. The performance of passive samplers to predict concentrations of these compounds in fish is as yet unclear. Bioaccumulation models for aquatic species at trophic levels up to and including predatory fish provide a mechanistic link between the concentrations in biota and concentrations in the water phase (Arnot and Gobas, 2003), although reliable species- and compound- specific BAF values are required, and these can be scarce or even absent (Arnot and Gobas, 2006). These considerations imply that setting water based thresholds for the protection of predators is in principle valid, but that biota sampling will be required to reduce the uncertainties in estimated concentrations in prey organisms. WKPSPD considered that biota based monitoring be supplemented by passive sampling whenever possible, because this would allow the generation of valuable data on field-based BAF values that would improve contaminant modelling at the higher trophic levels.

Passive sampling in biota tissue and extracted lipids is a recent application that allows for a direct assessment of chemical activity in the biota (Ossiander *et al.*, 2008; Jahnke *et al.*, 2008; Jahnke *et al.*, 2009; Mayer *et al.*, 2009; Maenpaa *et al.*, 2011). With this method, a polymer is equilibrated with a biota tissue, tissue homogenate, or lipid extract, either by immersion or via a headspace. Typical equilibration times are in the order of hours (Ossiander *et al.*, 2008; Mayer *et al.*, 2009; Jahnke *et al.*, 2009) for PCBs and PAHs in fat rich tissues. Contaminant concentrations in the polymer are directly proportional to the chemical activity, and comparison of these concentrations therefore allows for directly comparing chemical activities among species without the use of lipid normalisation or knowledge of bioaccumulation factors. Combining this method with passive sampling of sediments makes it possible to assess whether contaminated sediments are a source or a sink for pelagic species (Jahnke *et al.*, 2012).

The short equilibration times for PS exposures in sediments and biota triggered a discussion on whether concentrations in a reference polymer phase should be used as a proxy for chemical activity, as a replacement of concentrations in the water phase (Maenpaa *et al.*, 2011; Jahnke *et al.*, 2012) (see Sections 7.1.1 and 7.1.2). It was noted that from a scientific viewpoint both proxies are equally sound, that concentrations in water (C_{free}) and in a reference polymer (C_{polymer}) are linked via the polymer-water partition coefficient, and that practical and conceptual considerations are decisive.

An advantage of using C_{polymer} is that it is more directly linked to experimental measurements, and needs no conversion to C_{free} using polymer-water partition coefficients, which often carry a large uncertainty. The use of C_{polymer} requires that the reference polymer is well defined and universally available, also in the future. However, concentrations in any polymer, can be converted to the reference polymer, using polymer-polymer partition coefficients, which are smaller than polymer water partition coefficients, and therefore easier to measure. The discussion on the use of a reference polymer was carried another step further, by considering that the concentrations in a reference lipid such as triolein can also be used as a proxy for chemical activity. Triolein has the advantage that it is a well-defined matrix that it is universally available at high purity, and that polymer-triolein partition coefficients are small and therefore easily determined. A further advantage is that expressing chemical activity on a triolein basis allows for a convenient comparison with lipid normalised concentrations in biota and thereby eliminates the conceptual difficulties that are associated with interpreting C_{free} . It was noted that equilibrium typically is not achieved with PS of water, and that the results for water sampling would have to be converted to equivalent concentrations in triolein using the triolein-water partition coefficient. Another consideration is that the use of polymers or triolein as a reference phase is only convenient for nonpolar contaminants, and that water remains a more convenient reference phase for polar chemicals and trace metals.

8 Session 5: Passive sampling/dosing and toxicity testing

8.1 Presentations

8.1.1 Craig Robinson: "Passive sampling and in vitro toxicity testing in Scotland."

Marine Scotland Science has used silicone rubber passive samplers to determine environmentally relevant concentrations of PAHs and PCBs, of water (e.g., Smedes *et al.*, 2007a; 2007b; 2007c) or of sediments (Yates *et al.*, 2011). Recently the range of compounds investigated was expanded to include PBDEs and less polar compounds such as alkyphenols, pesticides, and herbicides (e.g., Balaam *et al.*, 2011) – the latter have been analysed by partner laboratories and with either semi-quantitative estimates of sampling rates, or without calibration for sampling rates. Most recently, extracts of passive samplers have been used in a variety of *in vitro* toxicity testing systems in order to improve understanding of the potential of the contaminant burdens to cause adverse environmental effects in two contrasting environments (Emelogu *et al.*, 2013a; Emelogu *et al.*, 2013c).

Silicone rubber passive sampling devices (SR-PSDs) were deployed (7-12 weeks) at 5 sites in two localities of differing characteristics. The studied areas were the River Ythan and its estuary, and the estuary and Firth of Forth. The Ythan is a small, agriculturally-dominated catchment in NE Scotland, parts of which suffer from declining ecological status under the WFD classification scheme; the Firth of Forth is a major coastal inlet on the Scottish east coast that has potential sources of contaminants in the form of run-off and discharges from urban areas, industrial sites, including a major oil refinery and petrochemical complex, coal-fired power stations, and shipping.

Passive sampling for the determination of aqueous freely dissolved PCBs and PAHs followed ICES guidelines (Smedes and Booij, 2012), using PCBs and deuterated PAHs as PRCs, and GC-ECD (PCBs) and GC-MS (PAHs) analytical instrumentation. Additionally, concentrations of up to 47 pesticides and 22 acid and urea herbicides were determined in the silicone rubber samplers (ng/g) using GC-MS/MS and LC-MS/MS instrumentation respectively (Emelogu *et al.*, 2013a; Emelogu *et al.*, 2013c). At two locations on the River Ythan, continuous autosamplers were co-deployed with the SR-PSDs and composite water samples (6-8 weeks) were subjected to conventional pesticide (GC-MS/MS) and herbicide (LC-MS/MS) analyses. At all ten sampling sites, additional SR samplers were deployed in order to provide extracts for use in toxicity tests.

In order to improve understanding of the potential of the developed expertise and to introduce new techniques in a step-wise manner, initial toxicity testing was conducted using extracts of the silicone rubber samplers transferred to methanol or DMSO and exposed to cell lines or test organisms in a 24 well microtitre plate exposure system. Cytotoxicity (neutral red uptake assay) and cytochrome P450 enzyme induction (EROD activity) were determined in a rainbow trout liver cell line (RTL-W1) (Emelogu *et al.*, 2013b), effects on zebra fish were assessed using the Fish Embryo Toxicity (FET) test (Emelogu *et al.*, 2012), and effects on marine phytoplankton (*Pavlova lutheri*) assessed using the algal growth inhibition test (Emelogu *et al.*, 2013b). In a separate experiment, the silicone rubber O-ring passive dosing procedure described by Smith *et al.* (2010a) was used to expose the RTL-W1 cell line to two PAH compounds (chrysene, fluoranthene) loaded from a saturated solution with a dioxin (2,3,7,8-TCDD) as a positive control; cytotoxicity and EROD activity were then determined.

Freely dissolved PAH ($\Sigma_{n=40} = 27\text{--}70 \text{ ng L}^{-1}$) concentrations showed little variability between sites in the Ythan, and were similar to those determined in the estuary and Firth of Forth ($49\text{--}70 \text{ ng L}^{-1}$). PCB concentrations were higher in the Forth ($\Sigma_{\text{ICES-7}} = 70\text{--}130 \text{ pg L}^{-1}$) than the Ythan ($3\text{--}30 \text{ pg L}^{-1}$), reflecting the greater population density and number of historical contaminant sources in the Forth catchment. At each site in the Ythan, 36–39 pesticides (of 47 in the method) and 4–8 acid/urea herbicides (of 22) were detected in the SR-PSD, whilst analysis of simultaneously obtained composite water samples failed to identify any pesticides present, although 5–6 herbicides were detected. From the estuary and Firth of Forth, 4–6 pesticides and 1–4 herbicides were detected in SR-PSDs.

SR-PSD extracts from the Ythan were not cytotoxic to rainbow trout liver cells, but from all sites they induced CYP1A activity; this activity was much greater than that predicted from applying Toxic Equivalency Factors to determined concentrations of PAHs and PCBs. Three of the Ythan sites (the two on the stream failing WFD ecology, and the estuary) also showed toxicity in the Fish Embryo Test. Extracts from the Forth were subject to the algal growth inhibition test, and whilst all showed some activity, the level of growth inhibition was low.

Passive dosing of RTL-W1 cells showed that chrysene was cytotoxic and induced EROD activity, whereas fluoranthene was cytotoxic, but did not induce EROD activity.

To summarise, SR-PSDs were shown to sequester semi-polar compounds with $\log K_{ow}$ down to ~ 1.5 , as well as PAH and PCBs, and to capture information on many more compounds than could be obtained from continuous autosamplers. Extracts of SR samplers were shown to dose-responsively induce the activity of cytochrome P4501A detoxification enzyme in fish liver cells and to inhibit algal growth, without being cytotoxic. Coupling of passive sampling with *in vitro* toxicity tests can be used to improve understanding of the nature of pollutant pressures, and the coupling of passive sampling with passive dosing may provide a way to assess the significance of complex mixtures of non-polar and semi-polar contaminants sampled from the environment.

8.1.2 Els Monteyne: “The role of passive dosing in the Belgian monitoring program.”

Samplers that were exposed in 3 harbour stations, were used in toxicity tests as passive dosing devices. Two kinds of toxicity tests were conducted: a 24 h larval development test and a 72 h growth inhibition test with the marine diatom *Phaeodactylum tricornutum*. Water samples were analysed for PCBs, PAHs, PBDEs, organotins, organonitrogen pesticides, pharmaceuticals, phenols and phthalates. The results showed a link between actual environmental measurements and toxicity. The theoretical contribution to the mixture toxicity showed that pesticides, PAHs and organotins were responsible for at least 90 % of the mixture toxicity at all sampling stations. To conclude, passive samplers seem to be a very powerful tool for monitoring hydrophobic pollutants and linked to eco-toxicological assessment criteria, passive samplers could be the answer to current problems in monitoring of the marine environment.

8.2 Discussion on passive sampling/dosing and toxicity testing

The two presentations on toxicity testing were in relation to **passive sampling and assessment of water quality**. In the first, passive samplers were extracted and the extracts used for toxicity testing (see also Emelogu *et al.*, 2013a; Emelogu *et al.*, 2013c),

in the second, the passive samplers previously deployed in Belgian harbours (Monteyne *et al.*, 2013) were themselves used to passively dose toxicity tests. Both allowed an assessment of the (potential) biological effects of complex mixtures of unknown contaminants of environmental origin that summation of toxic potentials of known compounds measured in the sample does not allow, and furthermore included assessments of time-integrated sampling which traditional toxicity tests of spot sampled water do not allow. Dialysates from SPMDs have also been used in connection with chemical analyses and in vitro bioassays to investigate concentrations and effects of PAHs in water (Rastall *et al.*, 2004; Harman *et al.*, 2010). In the studies of both Emelogu *et al.* (2013c) and Harman *et al.* (2010), the induction of CYP1A (EROD) activity by planar organic contaminants in the bioassays was much lower than was predicted based upon the determined PAH and PCB concentrations; the study of Monteyne presented to WKSPD demonstrated that mixture toxicity to oyster embryos was >90% explained by the presence of PAHs, organotins and pesticides sequestered by the silicone rubber used as passive samplers/dosers.

Since the studies above used passive sampling of water, equilibrium would probably not have been attained except for the less hydrophobic compounds (typically compounds of $\log K_{ow} > 5.5$ do not attain equilibrium within the duration of passive sampling studies, i.e. weeks/months). If equilibrium is attained in the field, then concentrations in passively dosed toxicity tests will match those of the environment, allowing assessments of environmentally realistic complex mixtures. However, since equilibration times increase with increasing hydrophobicity, the concentration of the more hydrophobic compounds in the toxicity test will often be lower than in the environment being examined, which hinders the interpretation of the data, as concentrations and mixture compositions do not necessarily reflect the real-life situation. If total extracts of passive samplers are subject to toxicity tests, rather than using partition-driven equilibrium (passive) dosing, this situation becomes even less realistic. Nonetheless, the combination of water PS with toxicity testing provides additional useful information regarding time-integrated concentrations and their potential for biological effects in water (e.g. through effects directed analysis), as it combines the exposure to the contaminant mixture in a controlled laboratory situation.

Partition-controlled (passive) dosing of hydrophobic compounds either singly or in combination results in very stable and highly reproducible exposure conditions for hydrophobic compounds such as PAHs (e.g., Mayer and Holmstrup, 2008) and can be used to robustly dose tests on small organisms such as springtails, (Mayer and Holmstrup, 2008; Smith *et al.*, 2010b), larger organisms such as fish in flow-through conditions (Adolfsson-Erici *et al.*, 2012), or cell culture tests in microtitre plate format (Smith *et al.*, 2010a). The approach maintains stable mixture composition (Smith *et al.*, 2013; Schmidt *et al.*, 2013) by overcoming problems associated with differential rates of compound loss (through volatilisation, or sorption) in traditional mixture tests. Passive dosing has demonstrated that baseline toxicity of PAH mixtures is additive and can be predicted from the sum of the individual chemical activities within the mixture exposure (Smith *et al.*, 2013). Furthermore, mixtures of compounds at concentrations which do not individually cause baseline toxicity can be toxic, with a potency predictable from the summed chemical activity of the individual components in the mixture (Schmidt *et al.*, 2013).

Passive sampling/dosing of polar compounds and metals. WKSPD considered that PS of polar compounds is not sufficiently developed for compliance purposes (Section 5 above) whilst what exactly is being measured during PS of metals can pose problems in relation to EQS values. Furthermore, toxicity testing of these compounds

is best achieved through existing methods based upon dissolving the substances in water. For environmental assessment purposes, TWA metal concentrations can be obtained via PS and the concentrations reproduced accurately during traditional laboratory tests.

Passive sampling and assessment of sediment toxicity. Since passive sampling of sediments operates in the equilibrium phase over a wide range of $\log K_{ow}$ (see Section 6 above), combining this with passive dosing may produce a robust method of assessing the risk to organisms from the HOC mixtures that sediments contain, with fewer of the confounding factors that can be present when doing existing whole sediment bioassays (anoxia, hypoxia, variable physicochemical composition between sediments, etc.). Through PD of bioassays with internationally recognised assessment criteria (e.g. Tisbe copepod, oyster embryo or sea urchin embryo bioassays for which OSPAR BACs/EACs have been defined; Davies and Vethaak, 2012), this approach could be readily standardised and should be suitable to provide status assessments of sediments with respect to HOCs. Adding relevant concentrations of metals to the test media may also allow the porewater concentration of these to be included in the mixture assessment.

Environmental Management. In discussion, WKPSPD considered that SR O-rings could be placed in the field and then used for dosing in vitro toxicity tests since disinfecting them with ethanol could be done without extracting a significant proportion of the collected compounds. The workshop acknowledged the usefulness of being able to assess the significance of environmental mixtures, but also recognised that in the event of samples causing “harm”, further investigations would be required, for example through effects directed analysis, in order to identify causative agents for which measures could then be introduced by environmental regulators. In order to accurately assess environmental status based on PS/PD approaches, a careful choice of bioassay(s) is required. Whilst a sample may not cause toxicity in one assay or organism, it may be toxic in another test, raising the question of how many assays would be required in order to provide sufficient confidence that a sample/site is safe/of good status. There is no simple answer to that question, being a balance between cost and the information gained, but WKPSPD considered that several should be conducted to cover a range of taxa (e.g. algae, invertebrates, and fish).

9 Conclusions

Passive sampling (PS) is suitable for monitoring of nonpolar contaminants in aquatic environments (water, biota and sediment), with several benefits over existing techniques. PS of polar contaminants, although useful for investigative monitoring, is not sufficiently mature to be applied for compliance monitoring, whilst the suitability of passive metal sampling needs to be evaluated separately.

It ought to be relatively easy to progress PS to the point where it is acceptable for use within the OSPAR and HELCOM monitoring programmes. The further development of passive sampling of nonpolar contaminants would benefit from the addition of this method to OSPAR's pre-CEMP.

Although PS should be preferred to spot water sampling, hurdles currently exist in EU regulations and environmental management that prevent the use of PS for WFD compliance monitoring, although it can be used for investigative monitoring and in trend monitoring.

Sampler-water partition coefficients should be determined for compounds where these are lacking, and refined for those compounds for which the uncertainty around existing values is large. Guidelines for the determination of these partition coefficients need to be summarised and evaluated.

The development of a proficiency testing scheme for passive sampling of nonpolar contaminants is needed to improve the performance of monitoring laboratories for this technique and to produce reliable values of inter-laboratory uncertainty.

Assessment criteria (BACs and EACs/EQs) for PS (suitable for both water and sediment) should be defined in terms of C_{free} and a specific uncertainty target should be defined under the WFD for the combined uncertainty on C_{free} determinations.

Passive sampling of nonpolar compounds in sediments is straightforward, of direct toxicological relevance and avoids the difficulties associated with normalising total concentrations for sediment characteristics. Data should be reported as (porewater) C_{free} for comparison to the assessment criteria of C_{free} mentioned above.

Guidelines for passive sampling in sediments need to be developed. Such guidelines should cover the issues of depletion and equilibrium attainment, among others.

As a minimum, passive sampling results for water and sediments should be reported as C_{free} . Reporting concentrations on the basis of a reference polymer or model lipid has some merit, but would require the definition of a standard lipid (e.g., triolein) or reference polymer, the determination of lipid-water partition coefficients for the compounds of interest, and a redefinition of EACs/EQs in terms of concentrations in these reference phases.

Passive sampling is probably better, and more practical, than biota monitoring for the purposes of both trends and compliance checking. It allows an assessment of contaminant pressure (i.e. chemical activity, as indicated by C_{free}), and does not have the many confounding factors associated with biomonitoring. However, the capability of PS to predict concentrations in prey organisms is as yet unclear. It can be expected that parallel PS and biomonitoring will provide additional insights on (field based) bioaccumulation factors and contaminant transfer within the food web. Monitoring for human safety assessments (e.g. MSFD Descriptor 9) will continue to require the collection and analysis of biota.

Passive dosing (PD) of hydrophobic compounds, either singly or in combination, results in very stable and highly reproducible exposure conditions for hydrophobic compounds and predicts baseline toxicity of mixtures from the sum of the individual chemical activities within the mixture exposure.

The use of passive sampler extracts with *in vitro* toxicity tests can be used to improve understanding of the nature of pollutant pressures, and the coupling of PS with PD should allow assessment of the significance of complex mixtures of non-polar and semi-polar contaminants sampled from the environment.

The use of PS in water followed by PD in toxicity tests results in an underestimation of the effects of substances with $\log K_{ow} > 5.5$, since these compounds rarely attain equilibrium during the sampling stage in water. However, by including the effects of unknown contaminants, this approach may be more informative than assessments based on concentrations of identified individual compounds.

The use of PS in sediments followed by PD in toxicity tests may provide a more suitable tool for risk and status assessments of sediments, although development of the approach is still in the research phase. PS of sediments operates in the equilibrium phase over a wide range of $\log K_{ow}$, whilst there would be fewer of the confounding factors which are present with whole sediment bioassays.

Assessments based upon the combination of PS/PD should employ more than one toxicity test in order to assess risk to different taxa and provide sufficient confidence that a sampling site is of good status.

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Annex 2: Agenda

Workshop on the Application of Passive Sampling and Passive Dosing to Contaminants in Marine Media (WKPSPD)

ICES Headquarters, Copenhagen, Denmark

29–31 January 2013

1. OPENING OF THE MEETING

The meeting will begin at 13:00 on the first day, and at 9:00 thereafter

Welcome, housekeeping (safety, lunch, dinner)

Introductions / areas of expertise

ToRs, ICES requirements / expectations, report format / outline, any other presentations

Appointment of topic leads and rapporteurs

2. Session 1: COMPLIANCE MONITORING

2.a Presentations

- Paul Whitehouse (by webex): "EQSs for controlling toxic substances under the Water Framework Directive: challenges in implementing biota standards"
- Peter Lepom: "Passive sampling in regulatory monitoring – Opportunities and limitations."
- Martin Mørk Larsen: "PS and the monitoring requirements of OSPAR and HELCOM."
- Uta Kraus: "Testing and validation of passive samplers for monitoring priority organic pollutants for WFD, MSFD, HELCOM and OSPAR."

2b. Discussion

How does passive sampling meet or not meet the legal requirements of the regional seas conventions, and the European Union's legal requirements. What research needs and knowledge gaps can be identified.

3. Session 2: PASSIVE SAMPLING OF MARINE AND TRANSITIONAL WATERS

3.a Presentations

- Els Monteyne: "The role of passive sampling in the Belgian monitoring program"
- Jan Brant: "Use of passive sampling devices for surveys and monitoring in UK waters."
- Ian Allan: The state of the art with polar samplers

3.b Discussion

Present status of passive sampling technology for water, research needs; potential monitoring designs.

4. Session 3: PASSIVE SAMPLING OF SEDIMENTS

4a. Presentations

- Philipp Mayer, Kimmo Mäenpää, Annika Jahnke & Gesine Witt: "Equilibrium sampling of hydrophobic organic pollutants in sediment."
- Foppe Smedes: "Compounds in silicone rubber passive samplers equilibrated with marine sediments."
- Philipp Mayer: "Conclusions from the Pellston workshop on bioavailability/bioaccessibility measurements using passive sampling devices for the management of contaminated sediments."

4b. Discussion

Present status of passive sampling in sediments, research needs, monitoring design

5. Session 4: LINKING PASSIVE SAMPLING TO CONCENTRATIONS IN BIOTA

5a. Presentations

- Foppe Smedes: "Surface water passive sampling and concentrations in biota."
- Philipp Mayer, Stine N. Schmidt, Annika Jahnke, Kimmo Mäenpää: "Calibrating passive sampling and passive dosing techniques to lipid based concentrations."

5b. Discussion

Present status of linking passive sampling to concentration in biota. Can passive sampling complement or even replace biomonitoring?

6. Session 5: PASSIVE SAMPLING/DOSING AND TOXICITY TESTING

6a Presentations

- Craig Robinson: "Passive sampling and in vitro toxicity testing in Scotland."
- Els Monteyne: "The role of passive dosing in the Belgian monitoring program."

6b. Discussion

Passive dosing: state of the art, research needs, links to MSFD Descriptor 8 ("harm"), role of passive sampling/dosing in toxicity testing

7. GENERAL DISCUSSION

8. CLOSURE OF THE MEETING

The meeting will be closed at the third day, 13:00

Annex 3: WKPSPD terms of reference

Workshop on the Application of Passive Sampling and Passive Dosing to Contaminants in Marine Media (WKPSPD)

2012/2/SSGHIE01 The Workshop on the Application of Passive Sampling and Passive Dosing to Contaminants in Marine Media (WKPSPD), co-chaired by Craig Robinson*, UK, and Kees Booij*, NL, will be held at ICES Headquarters, Copenhagen, Denmark, 29–31 January 2013 to:

- a) Report to ICES on current experience of the use of Passive Sampling in the (marine) environment and Passive Sampling and Passive Dosing in the laboratory
- b) Report to ICES on the practical application of Passive Sampling (PS) and Passive Dosing (PD) in compliance monitoring and assessments (WFD, MSFD and Regional Seas Conventions). Relevant issues encompass:
 - i) Evaluate current knowledge for its practical applicability;
 - ii) Investigate ways to link 1) passive sampling measurements to concentrations in biota (chemical monitoring) and 2) potential environmental effects (biological effects monitoring);
 - iii) Investigate how a monitoring system based on PS/PD could be conceived;
- c) Consider the legal aspects of monitoring with PS/PD e.g. compliance checking, uncertainties and the reliability in court;
- d) Describe research needs and challenges in relation to Passive Sampling and Passive Dosing in marine assessment based on a), b) and c).

WKPSPD will report by 22 February 2013 (via SSGHIE) for the attention of SCICOM and ACOM.

Supporting information

Priority	Passive Sampling (PS) and Passive Dosing (PD) are emerging as attractive alternatives to presently used methodologies for the assessment of marine environmental quality, and are relevant to the implementation to the Marine Strategy Framework Directive Descriptor 8 (Contaminants) and their effects.
Scientific justification	<p>There is on-going progress in the development of PS and PD and in particular on nonpolar compounds but many uncertainties remain. Difficulties with polar compounds are huge for PS as well as for PD.</p> <p>The activities of this Workshop will be a natural continuation of previous work in ICES expert groups. Several ICES advices in recent years have pointed to Passive Sampling and Passive Dosing as promising alternatives to present approaches for monitoring of contaminants in sediments. The Workshop is needed to provide the concentrated collaborative effort needed to move the topic forward across the environmental disciplines available to ICES, and to lay a clear foundation for future Guidelines. The WK will move the process forward at an important time in the implementation of MSFD and the redesign of the Regional Seas monitoring programmes.</p>
Resource requirements	The activities which provide the main input to this group are already underway, and resources are already committed. In order to ensure an efficient planning and leadership of the WK two co-chairs are needed.
Participants	The WK is expected to attract 15-20 experts.
Secretariat facilities	None
Financial	No costs identified

Linkages to advisory committees	SCICOM and ACOM
Linkages to other committees or groups	Passive sampling in marine sediments has been discussed for a few years in WGMS, and also, to a lesser degree, in WGBEC. Passive sampling in water has been addressed by both MCWG and WGMS. WGMS in collaboration with the MCWG is expected to lead the further work which may lead to a TIMES guidelines.
Linkages to other organizations	The work of this group is relevant for the implementation of the Descriptor 8 work under the Marine Strategy Framework Directive and thereby directly relevant for the Regional Seas Conventions.

Annex 4: Recommendations

RECOMMENDATION	ADDRESSED TO
1. Develop Background/Low Concentrations and Background Assessment Concentrations for nonpolar contaminants that are expressed as freely dissolved concentrations.	MCWG
2. Review published toxicity data for freely dissolved nonpolar contaminants, especially those derived from passive dosing experiments, aiming to evaluate their use as OSPAR Environmental Assessment Criteria (EACs) for passive sampling data.	WGBEC
3. Recommend the Working Group E for the Water Framework Directive to develop Environmental Quality Standards (EQSs) that are expressed as freely dissolved concentrations	OSPAR
4. Advise QUASIMEME and/or the association of Water Framework Directive Proficiency Testing schemes on the development of an exercise for passive sampling of nonpolar compounds in water and sediment.	MCWG
5. Update and finalise an earlier drafted document on passive sampling of nonpolar contaminants in sediments, for publication in the TIMES series.	WGMS/MCWG
6. Produce a TIMES publication on the determination of sampler-water partition coefficients and sampler-sampler partition coefficients, including their uncertainties.	WGMS/MCWG
7. Consider the WKPSPD recommendations in developing the sediment monitoring plan produced in 2013.	WGMS
8. Add passive sampling of nonpolar contaminants in water and in sediments to the pre-CEMP.	OSPAR MIME
9. Develop an OSPAR background document for passive sampling, taking on board the outputs by MCWG, WGMS and WGBEC on passive sampling.	OSPAR study group on passive sampling
10. In case passive sampling be accepted for inclusion on the pre-CEMP <ul style="list-style-type: none"> • encourage Contracting Parties to begin using passive sampling of nonpolar contaminants in their monitoring programs • ensure that all of the requirements of the CEMP (Background Document, ICES TIMES paper, Assessment Criteria and PT scheme) are in place before the start of the next Quality Status Reporting cycle 	OSPAR