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H. C. Andersens Boulevard 44–46
DK-1553 Copenhagen V
Denmark
Telephone (+45) 33 38 67 00
Telefax (+45) 33 93 42 15
www.ices.dk
info@ices.dk

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Executive summary

The Working Group on Marine Sediments in Relation to Pollution (WGMS) met from 8 to 12 March in San Sebastian, Spain. The meeting was chaired by Patrick Roose and Lucia Viñas and attended by 14 scientists from nine countries.

The proposed agenda was accepted without modifications and arrangements were made to carry out the work. For most topics, the group split up into subgroups that prepared the material for discussion in plenary. Furthermore, a number of informative and relevant presentations were given during the meeting. In particular, information on the use of passive samplers (PS), was presented through this means.

The group considered information relevant to the regionalisation of pivot values used for normalisation of contaminants in sediments. Based on the limited information available at the meeting, no significant differences between the pivot point values calculated for the differing Regions could be observed. The group recognises the lack of robustness of this initial evaluation and will continue work on this during its next meeting. WGMS recommends that the existing approach to normalization and pivot point values should continue to be used in assessments.

WGMS investigated how the uncertainty associated with the use of co-factors may impact data assessments. Unfortunately, the available data were too limited to reach firm conclusions. WGMS will continue to work on this at its next meeting and requested additional data to further this work. Also, the support of a statistician with expertise in assessment procedures is required and Dr. Rob Fryer will be invited to contribute to this work.

The preliminary background concentrations (BCs) for alkylated PAHs could not be reevaluated, as no new information became available. However, new information is expected by the next meeting in which case the process can be repeated. WGMS suggest that the proposed BCs are used such as they are, pending a new evaluation.

WGMS investigated the validity of the practice of using TOC (Total Organic Carbon) as a normaliser for organic contaminants in sediments, and, specifically if regionalised Koc values (organic carbon partition coefficient) are warranted. The discussion showed that that sediment sorption often cannot be described by a single Koc. Actually, the main interest for contaminant work is the bioavailable fraction (BAF) of contaminants. This fraction is mainly the result of sorbtion to simple amorphous OC (i.e., residues of humic and fulvic substances) that is not necessarily described by the Koc. WGMS recognises that PS techniques give a much better estimate of the BAF and will explore this alternative further, recognising the need to develop guidelines for this purpose.

Furthermore, WGMS felt that PS has a great potential in producing meaningful data on the status of the environment, also in the framework of WFD. The group will continue to focus on this topic, particularly in relation to sediments. The group further recommends that the earlier version of the guidelines describing PS of sediment by using silicone rubber (WGMS, 2007) are published as an ICES TIMES paper and to start the development of a more general set of guidelines.

Finally, WGMS contributed to the finalisation, in collaboration with MCWG, of the OSPAR Technical Annexes for monitoring of PFOS in sediments and for monitoring of dioxins in sediments.

1 Opening of the meeting

The 30th meeting of the Working Group on Marine Sediments in relation to Pollution was opened by Lorenzo Motos, Head of the Marine Research Division of AZTI, Spain. After a very informative presentation on AZTI, he welcomed the WGMS and wished everybody a pleasant stay and fruitful meeting.

2 Adoption of the agenda

After briefly going through it, the agenda was accepted with minor modifications, which are reflected in the report, and arrangements were made to carry out the work.

3 Review and comment on the report of the 2009 meeting of OSPAR/MON in relation to sediments.

OSPAR/MON did not meet in 2009 hence no assessment was available at the meeting.

4 Review information relevant to the regionalisation of pivot values and background concentrations of contaminants in sediment

Claire Mason introduced a study being completed in the UK which aims to derive regional baseline concentrations for use in assessment of trace metal concentrations at dredge disposal sites, using the principals of normalization as advocated by the WGMS in 2009 and described in OSPAR 2008. Thirty grain size-fractionated samples ($>63\ \mu\text{m}$), from 8 defined regions around England and Wales, were digested using HF and analysed for trace metal concentrations, including co-factors. Preliminary assessment shows that for most metals (except As) there was little variation from the current pivot point used by OSPAR MON. For As, the local pivot point was higher than the OSPAR pivot point for nearly all regions. This study is still in early stages and is due to be completed before the 2011 WGMS meeting, when a full update is planned.

Pivot values represent the concentrations of contaminants and cofactors in sediment containing no fine-grained material (i.e. in sand) and are used in normalization procedures as recommended by OSPAR 2008. Concerns were raised at WGMS 2009 that pivot values may change if the composition of sand-sized material differed significantly between different parts of the Convention area. The use of inappropriate pivot values could have significant impact on the calculated normalised concentrations, particularly for sediment samples containing relatively small proportions of fine-grained material. WGMS2009 therefore endorsed earlier recommendations (OSPAR assessment manual) that CPs be invited to present proposals for pivot values appropriate to particular parts of the Convention area, and recommended that such regionalised pivot values should be applicable over large parts of the Convention area.

Members present at WGMS2010 reviewed the available information and compared the current pivot values with their uncertainties. Access to the required information (concentrations of contaminants and cofactors in sediment containing no fine-grained material, i.e. in sand) was limited and many members did not have the analytical uncertainty data required to calculate pivot point confidence intervals. Metals concentrations for coarse sediments (defined here as containing less than 5% silt/clay

(<63 μ m) or maximum 2% <20 μ m) were available from three OSPAR regions and it was decided that this could be used to investigate possible procedures for assessing whether regionalization was required, with the recognition that there were certain limitations to the data set that should be addressed prior to a more in-depth investigation at the next WGMS meeting. The UK and Spain are both completing sample analysis currently and will have more comprehensive datasets available next year; additional data is also expected to be available from Germany and France.

The available data were sorted according to which OSPAR region they were sampled from, since in 2009 the WGMS advised that regionalised pivot values should be applicable over large parts of the Convention area, for example across entire Regions, or to all monitoring data from a particular country. If high variability of pivot point in the OSPAR region was shown, then it was agreed that location with the region should be included in this test. It would then be possible to test whether there was a need for different regional boundaries.

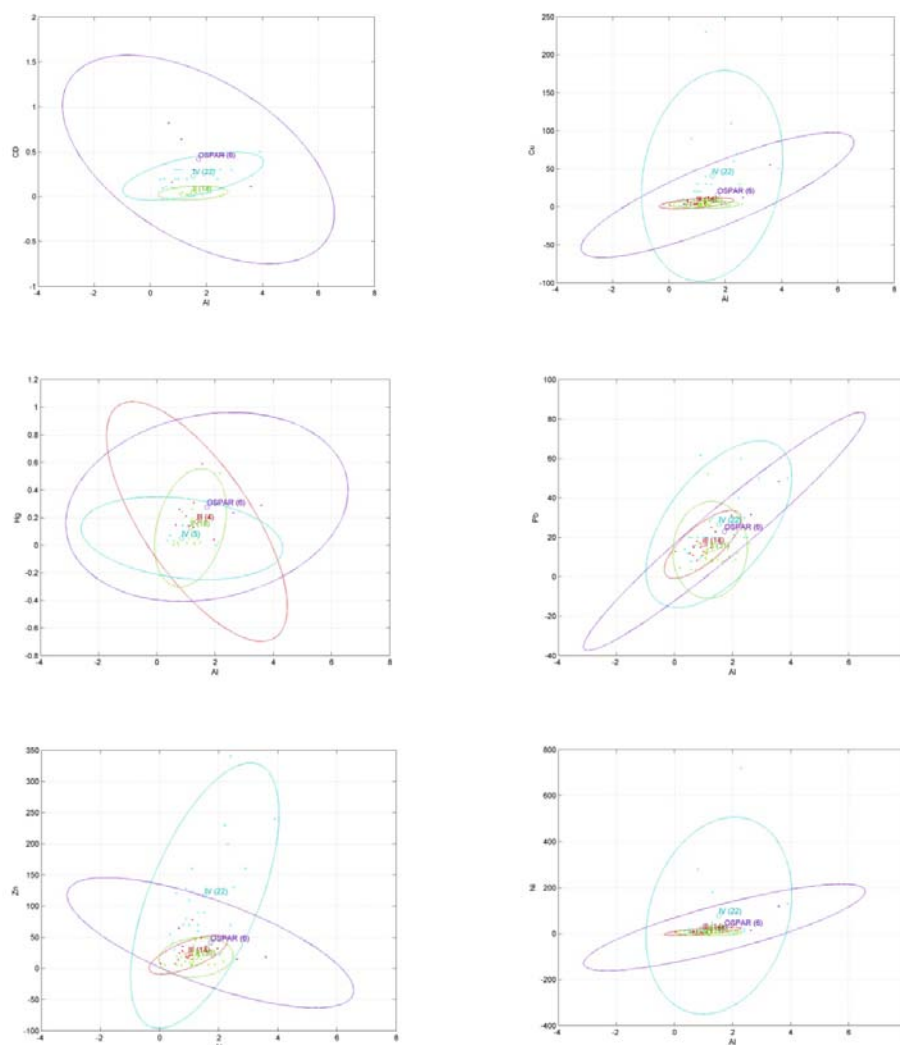


Figure 4.1. Pivot values (Cd, Cu, Hg, Ni, Pb, Zn / (mg/kg) against Al / (%)). Each differentiated region is represented by one individual colour, the mean pivot value (circle), the name of the region and the number of observations in brackets. All used individual measurements are indicated by dots.

The variability was addressed using a simple confidence interval approach. For each OSPAR Region (and the original data used to calculate the OSPAR pivot point values) the mean and 95% CI were calculated for contaminant and co-factor concentrations. Mean contaminant concentrations were then plotted (Figure 4.1) against co-factor (Al), with the mean for each Region being the pivot point for that area. Individual data points were also plotted. Where the confidence interval ellipses overlap, there is no statistical difference between the pivot points of those Regions. The following graphs (Figure 4.1) indicate that there were no significant differences between the pivot point values calculated for the differing Regions. However, there were very large variances in some of the datasets, particularly from Region IV and in the original data used to calculate the OSPAR pivot point values. For some elements (e.g. Cd) this variability may be due to the limited dataset, but for others with larger datasets (e.g. Cu) it may come from other sources, such as intra-Regional differences in baseline geology, or analytical uncertainty. For these reasons, WGMS2010 recommends that additional data be used to further this work and that a statistician with expertise in this area be asked to develop a statistical tool that allows a robust evaluation of whether differing pivot point values are required for differing Regions, or sub-regions.

All WGMS members are invited to provide information in relation to pivot points and background concentrations, to allow further work on this issue next year. In particular, data are requested for trace metal and co-factor (Al, Li, TOC, TON) concentrations derived by total digestion of coarse sediments. If similar data are also available from grain size- fractionated (or partially digested) sediments this would also be helpful in making more accurate calculations of pivot points. In addition data used to produce the current pivot points and background concentrations, as used by OSPAR MON, will be used in conjunction with new datasets to further assess regional differences in pivot points and background concentrations.

In the absence of accepted new proposals, WGMS recommends that the existing approach to normalization and pivot point values should continue to be used in assessments.

5 To report on the uncertainty in data assessments arising from the selection of co-factors

WGMS2009 invited CPs to present proposals for the specification of co-factors to be used for the normalisation of concentration of particular contaminants in their monitoring data. The effectiveness of the normalisation would be assessed through its effect on reducing the residual variance about the time-series. WGMS2009 also recommended that the normalisers should be applicable over wide geographical areas, e.g. entire regions or all data from a country.

WGMS 2010 was asked to report on how the uncertainty associated with the use of co-factors may impact on data assessments. Limited data were available to WGMS2010 for this to be undertaken and the task was to be undertaken by a sub-group whose main focus was on whether there may be a requirement for regional normalisation pivot points. It is recommended that this issue be addressed at WGMS2011 and that representatives bring suitable time-trend data to WGMS2011 and that a statistician with experience of the assessment procedures be invited to WGMS2011 to assist with addressing this important issue.

WGMS2010 repeats the invitation from WGMS2009 for CPs to bring forward proposals for the use of alternative co-factors. Such proposals should be supported by evidence that the use of an alternative co-factor (or no cofactor) reduces variability in the dataset. The first step should be to demonstrate significant differences in the correlations between each co-factor and the fine-fraction (<20 and <63 μm) of the sediment, and for correlations between contaminant and each co-factor. Use of an alternative co-factor would be recommended where there was a better correlation between co-factor and the fine fraction or contaminant. If assessment variability is significantly reduced for regions, then WGMS would recommend the calculation of Background Concentrations and Background Assessment Concentrations based upon co-factors other than Al; these should be applicable to large parts of the Convention area, such as entire OSPAR or MSFD regions. Existing approaches should be used in the absence of agreed alternatives.

French data were presented showing the relationships between concentrations of contaminants and co-factor (Al) for 94 stations from the Bay of Biscay (B. Boutier *et al.*, Metal contamination in the sediments of the Bay of Biscay, Ifremer, Bulletin RNO 2005, <http://wwwz.ifremer.fr/envlit/documents/bulletins/rno>). For clean stations, there were good linear relationships for most elements (e.g. Pb $r^2=0.84$), with outliers above this regression line being “contaminated”, or having differing base mineralogy. Regression against differing co-factors could be used to investigate whether those outlier data points were closer to the trend line and the variance was due to the mineralogy, or remained as outliers and were “contaminated”. However, this was not done at WGMS2010 and this baseline data will be made available to work with at WGMS2011.

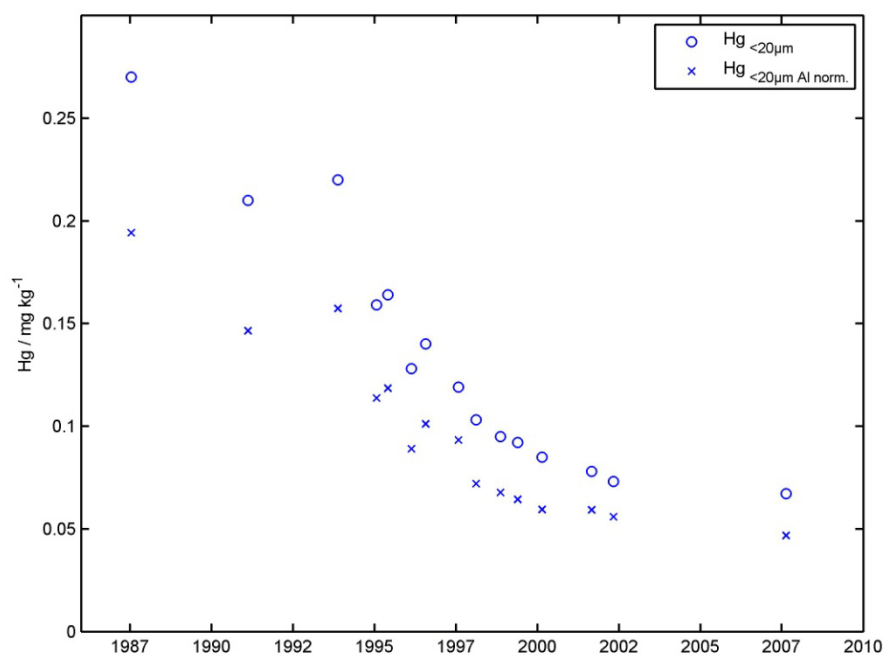


Figure 5.1. effect of normalising mercury concentrations from a German dataset to alumina in the <20 μm fraction.

Some German data were available suggesting that trace metals data from the <20 µm fraction does not require normalisation. As an example, Hg concentration data in the <20 µm fraction of a time series of 15 points had previously been plotted (Figure 5.1) as a time series using both the raw data, and using data normalised to 5% Al (not pivot point normalised). The time series have not been mathematically modelled, but the two datasets appeared to be parallel with little difference in variance.

WGMS2010 requests that additional data be obtained to further this work and recommends that a statistician with expertise in assessment procedures examine how the use or none-use of differing co-factors affects the assessments. The effectiveness of the normalisation would be assessed through the effect of application of normalisation on the residual variance about time series, as described in WGMS2009. In the absence of accepted new proposals, the existing approach should continue to be used.

6 Continue collection of data and develop background concentrations for alkylated PAHs

To address the OSPAR objective that concentrations of hazardous substances should be at or close to pre-industrial levels, Background Concentrations (and associated Background Assessment Concentrations; BCs and BACs) are required. Background Concentrations should be based on as much data as possible. As noted in the WGMS 2009 report, the BC values derived for alkylated PAHs (Table 6.1) have a very small basis due to the limited amount of available data. The WGMS 2009 encouraged CPs to collect more data and to include a wider geographical distribution than is presently the case. At the 2010 meeting of the WGMS no new data were available on concentrations of alkylated PAHs. However Celine Tixier reported that France had sampled new sediment cores in the eastern (Libyan South Coast) and occidental (Gulf of Lion, Rhone delta) Mediterranean Sea that will, among other contaminants, be analysed for alkylated PAHs. These data were bound to be available at the next years meeting. Although these data are outside the Oskar area they will extend the geographical coverage of the data set. Craig Robinson indicated that they had cores available for other purposes but would investigate if the deepest sediments from the core could also be analysed for alkylated PAHs. In addition to the above the WGMS continues to encourage CP's to collect more data.

WGMS suggest that the proposed background concentrations (Table 6.1) are used such as they are, pending a new evaluation as soon as more data becomes available.

Table 6.1 Background Concentrations of alkylated PAHs, expressed as concentrations normalised to 2.5% organic carbon.

PARAMETER	2008 PROPOSALS FOR BACKGROUND CONCENTRATIONS NORMALISED TO 2.5% ORGANIC CARBON
	(µG/KG DRY WEIGHT)
NAPC1	2.7
NAPC2	6.7
PAC1	2.7

7 Sediment dynamics

The paper "Sediment dynamics in relation to sediment trend monitoring" has been finalised, but is still in the process of being published as an ICES Cooperative Research Report. WGMS decided that no immediate actions will be taken on further reporting of the implications of sediment dynamics for the interpretation of sediment monitoring, because no new issues and data are currently available. If something new appears it can be added to the agenda for a future meeting under "any other business".

8 Passive sampling

8.1 Report ongoing and new projects involving passive sampling

Issues on the use and performance of passive samplers have been a focus area for WGMS for many years and presentations on ongoing projects were given by members of the group.

Natalia Montero from the hosting institute (AZTI Tecnalia) was invited to present the results of a study entitled Application of DGTs, mussels and TIE techniques for contaminant labile fraction evaluation, as an environmental assessment approach: an example in a Spanish Estuary (by Natalia Montero, Maria Jesus Belzunce, Joxe Mikel Garmendia, Joana Larreta, Izaskun Zorita and Javier Franco)

The study is part of a National Project which is being developed in an estuary of the Basque Country (North East Atlantic Spanish Coast). The study applies passive sampler techniques (Diffusive Gradient in Thin-Films: DGTs) and biomonitors (mussels) in order to evaluate the efficiency of monitoring technologies for determining the chemical status of waters according to the European Water Framework Directive (WFD; 2000/60/EC). Additionally, sediments under the water column are studied by means of Toxicity Identification and Evaluation (TIE) procedures to identify the chemicals responsible for toxicity. Efforts were centred on the three classes of contaminants that predominate in toxic sediments: ammonia, metals and organic compounds. Afterwards, toxicity reduction was proved by laboratory bioassays using a 10-day acute survival test with marine amphipods (*Corophium multisetosum*).

DGTs and transplanted mussels (from a clean area) were moored at four stations in Iartzun estuary in early May and in late June. Sediment samples were collected from the four stations by a Van Veen grab.

A pollution gradient was identified along the estuary using DGT and TIE techniques; these characterized the outer station as the least contaminated. However, based on the mussels results alone it is difficult to discriminate between stations because of the influence of abiotic and biotic factors in bioaccumulation. DGTs seem to be more reliable for representing metal distribution trends in highly variable water bodies. Differences in uptake between mussels and DGTs could be considered as species-dependent uptake differences. The combination of biomonitors with DGTs allows for obtaining different and complementary types of information about metal bioavailability. Moreover, based on the results obtained by DGTs and TIE, it can be concluded that those techniques that account for the 'labile' fraction of toxicants are a more realistic approach to toxicity than dissolved concentrations demanded by guidelines.

Some results are presented in Annex 3.

Claire Mason, on behalf of Jan Balaam, gave a short presentation about a current UK project, aiming to introduce passive sampling as a possible monitoring tool for use within the MSFD. The original plan aimed at achieving 45 sites in 15 areas, including inshore and offshore, and utilising the Smartbuoy network for offshore sites. Water sampling and three passive sampler types were employed: silicone rubber, POCIS (Polar Organic Contaminant Integrative Sampler) and SPATT (Solid Phase Adsorption Toxin Tracking) resin. Current priority substances, defined in the MSFD, were measured, with additional pesticides (methoxychlor, dicofol alachlor) and an alkylphenol (2,4,6-tri-tert-butylphenol). To date, 36 samplers have been deployed and retrieved, 36 silicon rubber samplers extracted, and the extracts from 29 silicone rubber samplers analysed. Qualitative analysis of 29 retrieved POCIS samplers has been completed. Many compounds could be measured using a single extraction, and there were measurable concentrations of most compounds found, both onshore and offshore, with contaminant gradients observed for many of them. There were smaller differences than usually observed between sites, and this is due to changing sampling rates. A step change in thinking is required to analyse these results in terms of 'allowable concentrations', and needs to link to biota concentrations AND effects. Analysis of the remaining Phase 1 samplers is continuing and Phase 2 of the project is currently underway, with additional passive samplers deployed alongside mussels and DGTs. The next steps are to complete the analysis of Phase 2 deployments, and to undertake in vitro biological effects (oyster embryo bioassay) testing using passive dosing via silicone rubber samplers; to establish a network of offshore sampling locations with deployment pre-approval; to determine silicone rubber partition coefficients (K_{sw}) for compounds not previously analysed, and to develop methodology to allow the extraction and analysis of additional compounds, particularly TBT.

Craig Robinson gave a brief presentation to update WGMS with new and existing passive sampling projects taking place at Marine Scotland.

Data were presented from two MSc projects (Chukwuemeka Ezeofor and Alma Balbayeva) that used silicone rubber water column passive samplers to investigate the composition and distribution of CBs and PAHs in the Firth of Forth and Firth of Clyde. Silicone rubber passive samplers were pre-extracted with ethyl-acetate, spiked with a mixture of 7 CB and four deuterated-PAH Performance Reference Compounds and deployed in May–June 2009 for 6 weeks at four locations along the Firth of Clyde, at seven locations in the Firth of Forth and two west coast sea lochs. In both Firths the locations were selected to include salinity ranges from nearly fully freshwater to fully marine. The recovered samplers were Soxhlet-extracted using acetone/iso-hexane (1:3), subjected to a preliminary C8 SPE clean-up and the extract split into a hydrocarbon and a CB fraction. For the hydrocarbon extract, aliphatic and aromatic components were separated by HPLC and 40 PAH compounds determined in the aromatic fraction by GC-MS; the CB fraction was passed through a deactivated silica column to separate CBs from most OCPs and 34 individual CB congeners (and 5 OCPs) determined by GC-ECD. The data presented were sampler concentrations and had not been corrected for sampling rate. Nonetheless, the distribution of PAHs and CBs in the Firth of Clyde were similar to those described in work undertaken in 2008, with highest concentrations found in the samplers from urban and industrial areas in the middle part of the transect, and lowest ones from outer Firth. Samplers from the urban/industrial sites also had larger proportions of 3- and 4-ring PAHs and tetra-chlorinated biphenyls than the cleaner areas. Samplers deployed in the Firth of Forth indicated a gradient of PAH, CB and OCP concentrations decreasing down the estu-

ary. Samplers located closest to the Grangemouth oil refinery had PAH ratio plots (methylphenanthrene/phenanthrene vs fluoranthene/pyrene) indicative of a petrogenic origin, with a gradual shift to more pyrolytic ratios towards the outer Firth; the most pyrolytic signature was from the Loch Etive sampler.

This year, Marine Scotland are starting a new project using in vitro silicone rubber passive sampling of dredged spoils that aims to develop tools for improving the suitability assessment of dredged material for sea disposal, and two new projects that aim to link passive sampling with biological effects responses. The first of these aims to link freely dissolved organic contaminant concentrations with biological effects observed in wild mussels at different levels of biological organisation (gene expression, DNA damage, whole organism response). The second aims to combine passive sampling with in vitro passive dosing of whole organism bioassays, reporter gene assays and gene expression in cell cultures in order to improve understanding of the relationship between contaminant concentrations and “harm”.

Céline Tixier gave a short presentation of an intercalibration exercise on passive samplers, which will take place in France in a few months (April-July 2010). This exercise is organized in the frame of the AQUAREF program (a consortium of five French institutes involved in water monitoring <http://www.aquaref.fr>). This Intercalibration exercise concerns expert laboratories involved in the development and deployment of passive samplers. The results will be disseminated to laboratories in charge of water monitoring. The main goal is to assess the potential role and efficiency of passive samplers for water pollutants measurements in surface water and coastal water. IFREMER is part of the organizing committee and proposes, besides two fresh water exposition sites, a marine site in a Mediterranean lagoon (Thau Lagoon). Several members of WGMS will take part in this exercise.

Per Jonsson, Sweden, presented a mass balance study of PCDD/Fs and PCBs in the Baltic Sea (Wiberg *et al.*, 2009; Cornelissen *et al.*, 2008; Armitage *et al.*, 2009) where passive samplers was used to measure the concentrations in the water mass and in the sediment pore water. The overall question was to examine and rank the important sources in the Baltic Sea and to help identifying measures to lower the concentrations of PCDD/Fs in Baltic fish. The passive samplers used were additive-free polyoxymethylene (POM) sliced to 1-cm wide and 17 µm thick strands. The strands were exposed in the field for 154–192 days to reach equilibrium with the water mass. To measure the pore water concentrations sediments were shaken in the lab with 2 g POM for 30 days. All strands were extracted with Soxhlet extraction before analysis.

It was concluded that the passive POM samplers worked well and were handy to operate even in offshore areas and at relatively large depths. The free concentration ratio between the sediment pore water and the overlying water of the open sea showed equilibrium conditions. The overall result of the mass balance was that the atmosphere is the major source of PCDD/Fs to the Bothnian Sea and the Baltic Proper.

Kristoffer Næs reported that numerous studies using passive sampling techniques have been performed in Norway the last years. These programmes address sediments as well as water masses and involve both measurements of metals and organic compounds. The objectives span from contaminant monitoring in industry influence fjords (Cornelissen *et al.*, 2009), assessing bioavailable fraction and uptake in benthic invertebrates (Ruus *et al.*, in prep.), basis for calculation of contaminant riverine inputs to marine waters and analyses for broad scale mass balances of emissions to Norwegian offshore waters. To that end passive samplers have been deployed in the Norwegian Arctic waters at Spitsbergen, the island of Jan Mayen and at Andøya (N-

Norway). Presently, passive samplers are also used to reveal contaminant release during benthic trawler-induced sediment resuspension (Allan *et al.* in prep.). Despite the regular occurrence of trawling activity, knowledge of the physical properties of sediment plumes is limited while even less is known of the possible changes in freely dissolved concentrations in the water column upon bottom sediment resuspension.

The WGMS discussed how to proceed with the passive sampling issue. The group felt that passive sampling has a great potential in producing meaningful data on the status of the environment and had the opinion that this would also be relevant for the WFD. Patrick Roose reported that the potential of passive sampling was communicated to the CMA (Working group on Chemical Monitoring Activities in relation to the WFD) but that it was not seen to be relevant yet, particularly for organic contaminants, since WFD regulations imply their measurement in total water, including SPM. Foppe Smedes reported that perhaps the passive sampling would enter the WFD as a replacement of biota monitoring since, for example, the presently used eels are now very scarce in the Netherlands. The Netherlands has already investigated how passive sampling results were related to concentrations in eel, fish and mussels, and the report acknowledged the potential of passive samplers to monitor the exposure of those organisms to contaminants. Furthermore, the Dutch National Institute for Health and Environment (RIVM) is investigating the use of passive sampling in the legal framework, as a second tier for situations where EQSs are not met.

There was agreement that WGMS would continue to focus on these methods and would have it as an agenda point on next year's meeting programme. The group will continue to report on projects that involve passive sampling and by that means explore the usefulness in the application of these methods.

WGMS also revisited the draft guideline for In-Vitro Passive Sampling (IVPS) of sediments (WGMS 2007, Annex 9). This guideline describes passive sampling of sediment using silicone rubber; it was produced on the basis of the ICES Passive Sampling Trial Survey and annexed to the 2007 WGMS report. This guideline gives a good description of the use of silicone sheets and films, and the group suggested that it could be published in the ICES TIMES series.

However the WGMS recognized that the guideline only considers the use of silicone rubber and applies only to the measurement of freely dissolved concentrations in the pore water.

Other materials can be also used and methodology to measure sorption isotherms is under development. With time it will be beneficial to develop a guidance document including the use of other materials and techniques in order to give a wider perspective on the passive sampling of sediments.

Foppe Smedes discussed in a presentation the mechanistic issues of passive sampling of sediments and made a first attempt to give perspective to the methodology of passive sampling. He also volunteered to (intersessionally) produce an outline of a document on passive sampling in sediments, with input from other group members and report this to the next WGMS meeting. The presently known mechanistic parameters that govern the passive sampling process were already collected during the meeting in a document that is attached as Annex 4. This includes also quality assurance on the passive sampling process, an issue that is already addressed in the guidelines for IVPS mentioned earlier.

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8.2 Undertake a review of partition coefficients for organic contaminants in sediments

The current data assessment methods used by OSPAR MON use TOC as the normaliser for organic contaminants. It has been suggested that this harmonised approach may not be appropriate for all parts of the Convention area since Koc's may vary from area to area.

WGMS therefore recommended in 2009 that the variability of Koc be investigated intersessionally, in order to assess the effectiveness of the normalization procedure and perhaps suggest regionalised approaches for normalization. However, the presentations to WGMS on passive sampling in sediments, particularly the presentation of Foppe Smedes, showed that sediment sorption often cannot be described by a single Koc. Equilibrations of sediment with passive samplers at different levels of extraction by passive sampling showed that, whilst there is a portion of the contaminants that is releasable, a residue of contaminants can remain in the sediment.

This is in agreement with the definition of (bio)availability by Reichenberg and Mayer (2006)¹ who defined bioavailability by two parameters: “chemical activity” and “accessibility”, as discussed in the WGMS 2009 report. The accessible concentration is releasable to the water phase and that leaves behind a concentration with no or limited accessibility in the sediment that is bound to “hard carbon” with much higher (orders of magnitudes) partition coefficients, or that is incorporated in the materials. Consequently, when the accessible concentration is released this less accessible fraction causes a much lower aqueous phase concentration that may not be significant at

¹ Reichenberg, F. and Mayer, P. 2006. Two complementary sides of bioavailability: Accessibility and chemical activity of organic contaminants in sediments and soils. *Environmental Toxicology and Chemistry*, 25(5): 1239–1245

all. The accessible, or releasable, concentration follows mainly sorption to simple amorphous OC, i.e. residue of humic and fulvic substances. Koc values reported in the literature are generally calculated from total sediment concentrations and can, therefore, be an overestimation with respect to the accessible concentration. On the other hand, calculation of the pore water concentration using the total sediment concentration and generic Koc values predicted from Kow will also result in an overestimation. The Koc for amorphous OC is likely to be closely related to the Kow, although Foppe Smedes showed in his presentation that Koc values of the accessible concentration still showed some variation.

In view of these uncertainties, the group decided that collecting Koc values from literature in support to the presently applied normalization procedures will not directly contribute to delivering further basis for spatial comparison of normalized values. Instead it is suggested to give highest priority to the development of passive sampling methods for the determination of the both aspects of bioavailability. That will, without doubt, allow a more meaningful spatial comparison of sediment contamination. Presently, assessment of sediments is done on the basis that a freely dissolved concentration (chemical activity) is proportional to the concentration in sediment expressed on the organic carbon content and the organic carbon – water partition coefficient (Koc) is assumed to be constant for a certain compound. The freely dissolved concentration can be measured directly through passive sampling as the primary measurement for comparison of sediments. This will also indicate if expressing contaminant concentrations on organic carbon is appropriate or needs to be revised. The secondary parameter will then be the measurement of the accessible concentration. Further action on this point will be part of agenda points on passive sampling and normalization activities. For the measurement of the freely dissolved concentrations in the pore water a guideline was finalized in 2007. Methods for the measurement of the accessible concentrations need to be evaluated to allow the development of guidelines. Measuring the both sides of availability will likely reveal if Koc values of the accessible pool, most important for the relations with the dissolved concentrations, will vary regionally or can be explained. The group decided that further action on this agenda point will be present on next year's agenda points regarding passive sampling and normalization activities.

9 Development of monitoring guidelines

9.1 Finalise the technical annex to the JAMP Guidelines for monitoring of dioxins in sediments

The annex was prepared as joint venture between members of WGMS and MCWG and discussed at the meeting of MCWG in the week before WGMS. The chair of WGMS presented the annex to the group and invited comments with the aim of finalising the document at the meeting. WGMS suggest that this annex still requires some of revisions. Clearly, the annex is based on a document for analysis of dioxins in biota, reflected by various references and the scheme at the end.

Comments and editorial suggestions were directly inserted in the text version available at the meeting. They can be summarized as follows:

- The subject requires proper definition: Polychlorinated dibenzo-p-dioxins and dibenzofurans;
- Avoid the use of brand names: replace Milli-Q water by ultrapure water;
- Most references to treatment can be omitted, this is a sediment guideline;

- Syringe standards is not a common name, use analytical or injection standard;
- Avoid unnecessary details: e.g. flow rates;
- Relative retention times are dimensionless;
- Table 5&6: add mass units;
- Some reference on biota could be removed;
- Adapt Figure 2 to sediments only.

These comments will be forwarded to the Chairs of MCWG and the authors, in order to finalise the technical annex.

9.2 Finalise the technical annex to the JAMP Guidelines for monitoring of PFOS in sediments

The annex was prepared by MCWG and already discussed at their meeting the previous week. WGMS was invited to comment the technical guideline with the aim of finalising the document for submission to OSPAR.

WGMS concluded that this is a very well written and useful document.

Some minor remarks were formulated:

- The IUPAC nomenclature for organic ends in –oate, not in –ate, this only holds for trivial names as acetate and butyrate, but ethanoate and butanoate are to be used;
- GC-MS is an appropriate detection technique as well;
- Checking for enhancement and suppression effects is mandatory for any technique. For this reason, the branched isomers cannot be assessed on the basis of linear isomer calibration, as the misestimate might be a manifold. This difficult problem must be tackled in a more sound way;
- Checking the calibration with a correlation coefficient >0.99 is not a good criterion;
- The blank defines the LOQ, not vice versa;
- The minimum peak height should be related to the LOQ, so only indirectly to the blanks.

These comments will be forwarded to the chairs of MCWG and the authors, in order to finalise the technical annex.

9.3 Finalise the technical annex to the JAMP Guidelines for monitoring of chlorinated biphenyls in sediment

The annex was prepared as joint venture between members of WGMS and MCWG and discussed at the meeting of MCWG in the week before WGMS. The chair of WGMS presented the outcome to the group and invited comments with the aim of finalising the document at the meeting. No new revision of the document was deemed necessary. It can be forwarded to ICES as it stands.

10 Provide expert knowledge and guidance to ICES Data Centre (possibly via sub-group) as requested

No questions were submitted to group.

11 Report to SSGHIE on your plans to promote cooperation between EGs covering similar scientific issues

WGMS has collaborated in the past, and during this meeting, with MCWG in the development of technical annexes, and will continue to do so in the future.

WGMS can collaborate with MCWG in any field where (novel) techniques or developments related to contaminants in sediments are brought forward.

WGMS2010 identified passive sampling as a scientific issue that can promote cooperation with two other EGs:

- MCWG (Marine Chemistry Working Group): to promote the use of passive sampling in the field of environmental monitoring, exposure assessment (availability of contaminants for diffusive exchanges);
- WGBEC (Working Group on Biological Effects of Contaminants): to develop further the use of this tool in an ecotoxicological perspective, for a better understanding of the link between exposure assessment (availability) and biological effect.

WGMS can also collaborate with the SGIMC in matters relating to sediment and the EG WGEIM where the impact of mariculture-derived contaminants on sediments is concerned.

12 Any other business

12.1 CMA guideline for sediment and biota monitoring in the WFD

The latest version of this guideline was presented to the group for their comments. Several members of the group have been involved in the preparation of this document and comments made by WGMS as a whole could therefore prove to be helpful both directly and indirectly in the further development of the guideline.

According to WGMS, the document has improved a lot since last year. WGMS elaborated on the comments from the review of the document by MCWG in the previous week. In general, they supported the comments made by MCWG. The right topics are addressed and a lot of time and effort has been spent to gather the information on different subjects and expertise domains. There are some general remarks that were made:

- Since the information had to be collected from different domains, there is need for harmonisation in both style of writing and order of topics. Several points are treated under various sections (often partly), whereas mentioning it once but thoroughly and referring to it afterwards is recommended. Repetition needs to be removed;
- Subsequently, the whole document needs to be revised by a native English writer;
- The authors want to make sure that relevant organisms and contaminants are monitored. Nevertheless, the readability must not be compromised; too much explanation is to be avoided as well;
- Some sections need proper rephrasing or have to be condensed;

- Although rare, some things mentioned are questionable or irrelevant and we recommend removing them (they are deleted in the document with track changes);
- Some sentences need verification, e.g. in OSPAR guidelines;
- Some terms need to be defined;
- References need proper crosschecking (some of them are not mentioned in the text).

Although, guidelines based on WGMS advice, are properly referred to in the document, the group fears their interpretation has not always been appropriate. As an example, the need to recalculate fine grained sediments e.g. from the Baltic Sea to 100% fines is not a proper interpretation of the guidelines on normalisation developed by WGMS. Also, the guidelines could take more recent advice into account e.g. the most recent guideline on normalisation developed by WGMS or the CEMP assessment manual 2008.

Generally, we believe that, taking these remarks into account, the document can become a valuable guideline.

12.2 The final TG8 report

The final version of the report produced by the ICES/JRC task group on MSFD Descriptor 8: "Concentrations of contaminants are at levels not giving rise to pollution effects", was submitted to the group for commenting.

The working group concluded that the paper summarizes important factors to be considered when evaluating sediment concentrations in relation to pollution effects. The working group recognised that the document is very general and lacks more specific recommendations to help the member states in describing the conditions in their marine environments.

However, WGMS found that ICES already has given comments to the Commission and that a new draft is already about to be prepared and to be presented to the member states. The group noted that although the ICES organisation involves an expert group on marine sediments in relation to pollution, the ICES comments have been forwarded to the Commission without consulting the WGMS.

12.3 Presentations

No specific further issues were raised under AOB but a number of informative presentations were presented and discussed under this topic. A short summary of these is given below.

Ingemar Cato gave a talk about the distribution of organotins in sediments from the Swedish continental shelf. Organotin compounds including tributyltin (TBT), are toxicants with a broad range of biocidal effects that have primarily been used as anti-fouling additives in ship paints. The compounds have been characterized as some of the most toxic substances ever released to the marine environment. Even in very small concentrations they can cause serious damage to marine life. The Oslo and Paris Commission (OSPAR) has set its environmental assessment criterium at 50 ng/kg dry weight. Also, both the EU-WFD and OSPAR consider organotins to be priority substances. Already in 2002, the Geological Survey of Sweden (SGU) started a project to follow up on the effects of the Swedish initiatives in 1989 (pleasure boats <25 m long) and 1993 (ships >25 m long) for banning the use of these substances. This

extensive work covering more than 200 sites along the Swedish coast and open sea has been conducted in order to identify the presence, distribution and breakdown of organotins in Swedish marine sediments. The results have shown that TBTs are present in the entire Swedish continental shelf area. The levels in sediment from some harbours and marinas are more than 300 000 times higher than the eco-toxicological threshold value mentioned above. That this poses a threat to marine life has been demonstrated in several collaborative projects by researchers from the University of Gothenburg. Examination of gastropods revealed a high incidence of imposex. In several marinas and harbours these gastropods have become extinct. TBT has been found in bladderwracks, blue mussels, eelpout and cod liver. Published results have been given a lot of attention as the studies among others demonstrated poor compliance with the prohibition of using these antifouling paints.

Germán Rodríguez, from the hosting institute (AZTI Tecnalia) was invited to give a presentation on the Determination of background levels of heavy metals in estuarine and coastal sediments of the Basque Country based upon the heuristic proposed by Reimann, Filzmoser and Garrett (2005); (Germán Rodríguez, Maria Jesús Belzunce, Ángel Borja, Javier Franco, Oihana Solaun, Itziar Tueros, Victoriano Valencia and Antoni Zuazo).

The determination of natural background levels of heavy metals in marine habitats can be useful to assess the degree of contamination in an specific area (e.g., Carballreira *et al.*, 2000). Metal concentrations (As, Cu, Fe, Hg, Mn, Ni, Zn) in surficial estuarine and littoral sediments of the Basque Country have been analysed in order to calculate the local background levels. The metal concentrations were measured in samples containing more than 10% mud fraction <63 µm (i.e., 575 samples). The metal concentrations were analyzed in the <63 µm fraction. The analysis of heavy metals was carried out by Atomic Absorption Spectrometry AAS in samples after acid extraction procedures (HCl + HNO₃). Due to the regional geological differences, some studies showed the convenience to derivate local background levels (e.g., Reimann *et al.*, 2005). Cluster analyses were carried out on data before the background values calculation. These cluster analyses did not differentiate among different areas (i.e., estuaries or sub geographical areas) or among different habitats (i.e., intertidal, estuarine or littoral). Therefore the background values were calculated on all the data set together.

The range of background variation and thresholds were calculated following the heuristic proposed by Reimann, Filzmoser and Garrett (2005). This heuristic is based upon the graphical inspection of the empirical data distribution and geographical displays. After removing areas with high percentage of outliers, Cd, Cr, Fe and Ni followed unimodal data distributions; whereas As, Cu, Mn, Hg, Pb and followed polymodal data distributions. For As, Cu, Mn, Hg, Pb the background variation and thresholds were calculated in basis of maximum likelihood mixture estimations (Carral *et al.*, 1992; Carral *et al.*, 1995), based in the NORMSEP program available in the FiSAT II package (Gayanilo *et al.*, 1996). This software allowed the identification of discrete Gaussian sub-populations within a data set. It is assumed that the subpopulation with the lowest average concentration is made up from the values corresponding to uncontaminated sites. The data distributions of Pb and Mn were not well adjusted by the maximum likelihood mixture.

The mean values of the background ranges found for As, Cd, Cr, Mn, Hg and Zn, fit well with the previous values provided for the Basque Country (Table 12.3.1). The

central background values of Cu, Fe and Ni, are higher than reported previously within the same region (Table 1).

Table 12.3.1. Range of background values determined in the Basque Country compared to central values (within the DLC, CPA, MLME approaches) or upper threshold (within the CFP approach) of metal background ranges, as reported in previous studies ($\mu\text{g g}^{-1}$) from the Basque Country (BC) and the Iberian Peninsula. Statistical approach: DLC=Dated Long Cores/vertical profiles; CFP=Cumulative Frequency Plots; CPA=Component Principal Analysis; MLME=Maximum Likelihood Mixture Estimation; and GD=Geographical Display. Analytical methodology: XRF=X-Ray Fluorescence spectroscopy; AAS= Atomic Absorption Spectroscopy; ICP/AES=Inductively Coupled Plasma Atomic Emission Spectroscopy; and DPASV=Differential Pulse Anodic Stripping Voltammetry (Table from Rodriguez *et al.*, 2006).

AUTHORS	AREA	ANALYTIC		SEDIMENT	AS	Cd	Cu	Cr	Fe	Mn	Hg	Ni	Pb	Zn
		STATISTIC	AL AP- PROACH											
This study	Basque Country (BC)	MLME+GD	AAS	<63 μm fraction	<0.05–24	0.05–0.45	2–64	<0.4–71	11,000–53,542	32–447	<0.03–0.27	2–57	<0.05–66	46–248
Cearreta <i>et al.</i> , 2000; Cearreta <i>et al.</i> , 2002	Nervion estuary (western BC)	DLC	XRF	bulk	16		19–20	76–85	25,000	300–400		20–23	21–23	60–63
Legorburu <i>et al.</i> , 1989	Gipuzkoa (eastern BC)	CFP	AAS	bulk		0.20	21	26	21,600	289		17	16	56
Sola <i>et al.</i> , 1990	Gipuzkoa (eastern BC)	CFP	AAS	bulk		0.24	15	23	9,100	232		12	23	
Borja <i>et al.</i> , 1996	Basque Country	CFP	AAS	<63 μm fraction		0.32	18	11	19,000	175	0.14	12	34	175
Carballeira <i>et al.</i> , 2000	Galicia (NW Spain)	MLME	AAS	<63 μm fraction			20–35	30–54	29,000–33,000	248–395		31–38	50–78	120–136
Cobelo-García y Prego, 2003	Ferrol Ria (NW Spain)	DLC	AAS	<63 μm fraction			12	63	24,000			26	27	55
Rubio <i>et al.</i> , 2000	Ria de Vigo (NW Spain)	CPA	ICP/AES	bulk			29	34	35,100	244		30	51	105
Riba <i>et al.</i> , 2002	Guadalquivir estuary (SW Spain)	DLC	AAS/DPASV	bulk		0.16–0.18	12–23		14,200–14,300	234–433			24	123–156

AUTHORS	AREA	ANALYTIC		SEDIMENT	AS	CD	CU	CR	FE	MN	HG	NI	PB	ZN
		STATISTIC	AL AP- PROACH	AL METHODO LOGY										
Blasco <i>et al.</i> , 2000	Barbate estuary and Bay of Cádiz (S Spain)	DLC	AAS	<1000 µm fraction			15–21	60–97	22,500–42,200	278–403				

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Sola, M. J., Alonso, B., Ramos, A., Cantón, L., and y Legorburu, I. 1990. Metales pesados en sedimentos del litoral de Guipúzcoa. *Sem. Quí. Mar.*, 5: 205–213.

German Rodríguez from the hosting institute (AZTI Tecnalia) was invited to give a presentation on Baseline of butyltin pollution in coastal sediments within the Basque Country (northern Spain), in 2007–2008 (Rodríguez *et al.*, 2010).

Tributyltin (TBT), dibutyltin (DBT) and monobutyltin (MBT) were analysed in 36 surficial sediments (upper 1 cm), at the ports of Pasaia and Bilbao, together with other mid- and small-size harbours of the Basque Country (northern Spain), in 2007–2008. Concentrations of MBT, DBT, and TBT were analysed in the bulk sediment fraction, using isotope dilution analysis with GC-ICP-MS (see Rodríguez *et al.*, 2010 for more details). The highest values of the sum of the three analysed butyltin species (up to 3,640 ng g⁻¹, as Sn) were found at sampling stations near to an active shipyard (sampling site Pasaia 26) and to another shipyard (sampling site Pasaia 31) that finished its activity in the '90s (both shipyards located within the port of Pasaia, see Table 1). The highest value of TBT concentration (3,143 ng g⁻¹, as Sn) was found at the marina of Getxo, in the port of Bilbao (sampling site Bilbao 11, Table 12.3.2). In sediment sampled in other marinas lower values of TBT were measured. The degree of TBT degradation was significantly correlated with redox potential and the TBT concentration (normalized by organic matter content). In some of the sampling points, imposex was evaluated in *Nassarius reticulatus* and/or *Nassarius nitidus* (see, for more details, Rodríguez *et al.*, 2009a; Rodríguez *et al.*, 2009b). A general and positive correlation was found between imposex degree and TBT content in sediment (Figure 12.3.1).

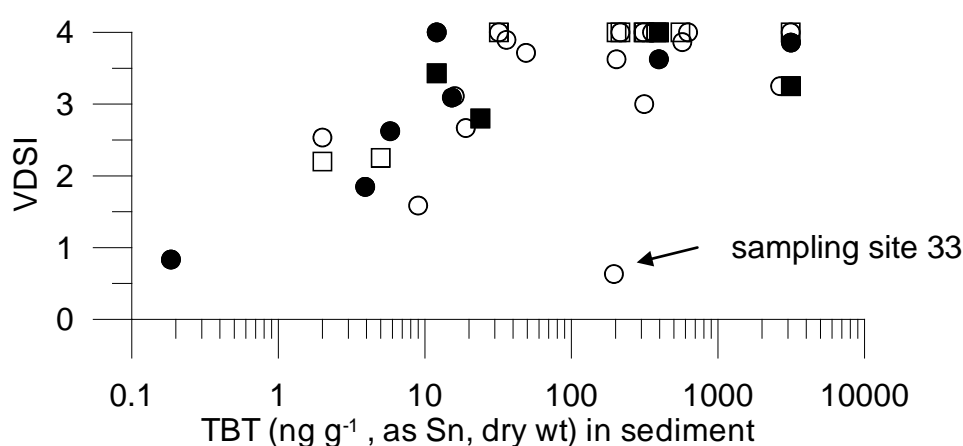


Figure 12.3.1. Relationship between TBT in sediment and VDSI (Vas Deferens Sequence Index) in *Nassarius reticulatus* (circles) and *N. nitidus* (squares). Imposex was evaluated in 2007, whereas some TBT in sediment was measured in 2007 (white points) and others in 2008 (black points).

Table 12.3.2. Concentration of tributyltin (TBT), dibutyltin (DBT), monobutyltin (MBT), and sum of butyltins (BTs, i.e., sum of TBT, DBT and MBT concentrations) in surficial sediments from the Basque Country (ng g⁻¹, as Sn, on dry weight basis). Key: Eh — redox potential; TOM — total organic matter; H — harbour; M—marina; F — fishing fleet; S — shipyard; O — open berth area. Table based in Rodríguez *et al.*, 2010.

LOCATION	SAMPLING	LABEL	DEPTH	TBT	MUD	Eh	TOM	TBT	DBT	MBT	BTs
	DATE		(M)	SOURCE	%	MV	%	NG G ⁻¹ , AS SN			
Zierbena	2007-02-01	1	5	H	78	-19	2.8	9	7	1	17
Algorta	2007-02-19	2	intertidal	O	0	495	1.8	2	7	10	19
Bilbao 3	2008-02-26	3	31	O	11	93	1.1	0.2	2	<0.1	2.2
Bilbao 6	2008-02-26	6	24	H	68	67	4.3	4	2	3	9
Bilbao 7	2008-02-26	7	23	H	59	41	3.8	6	4	3	13
Bilbao 8	2008-02-26	8	15	H	62	-63	5.2	15	6	3	24
Bilbao 9	2008-02-26	9	6	H,F,S	72	-32	6.8	395	59	11	465
Bilbao 10	2008-02-26	10	4	M	84	8	7.5	12	8	4	24
Bilbao 11	2008-02-26	11	7	M	90	-32	5.6	3143	131	39	3313
Bilbao 37	2008-02-26	37	8	H	64	-93	5.7	24	12	15	51
Bilbao 55	2008-02-26	55	3	M	68	-67	5.7	18	6	3	27
Bilbao 56	2008-02-26	56	8	H	79	-15	9.0	10	9	11	30
Bilbao 57	2008-02-26	57	6	H	77	31	8.0	7	10	8	25
Bilbao 58	2008-02-26	58	8	H	97	-4	9.2	9	9	7	25
Bilbao 59	2008-02-26	59	34	O	4	172	1.0	0.1	0.3	<0.1	0.4
Armintza	2007-02-01	13	2	M,F	69	-45	3.6	151	47	61	259
Plentzia	2007-02-20	38	1	M	74	-46	7.4	5	3	4	12
Lekeitio	2007-02-08	17	5	H,F	52	-81	6.4	19	16	8	43
Ondarroa	2007-02-08	41	6	H,F	76	-84	8.0	554	156	35	745
Mutriku	2007-02-13	16	6	H,F	76	-70	5.4	49	13	36	98
Zumaia	2007-02-08	60	1	M	69	-20	7.1	10	18	2	30
Getaria	2007-01-25	18	10	H,F	29	87	1.9	314	20	8	342

Pasaia 22	2007-04-20	22	12	H,O	29	101	2.9	625	2874	43	3542
Pasaia 23	2007-04-20	23	13	H,O	9	308	2.7	36	31	10	77
Pasaia 24	2007-04-20	24	13	H,F	52	9	12.2	571	145	20	736
Pasaia 25	2007-04-20	25	10	H,F	63	71	3.8	216	102	53	371
Pasaia 26	2007-05-11	26	9	H,S	60	22	10.3	3132	320	71	3523
Pasaia 27	2007-04-20	27	12	H,O	6	253	0.8	32	17	23	72
Pasaia 28	2007-04-20	28	11	O,S	41	8	6.4	203	64	58	325
Pasaia 29	2007-05-11	29	12	H	75	32	12.1	310	89	16	415
Pasaia 30	2007-05-11	30	9	H	71	28	11.3	355	106	42	503
Pasaia 31	2007-04-20	31	13	H,S	8	266	1.3	2655	985	0.1	3640
Pasaia 32	2007-06-13	32	14	O	1	426	3.0	16	3	33	52
Pasaia 33	2007-06-13	33	15	H	7	63	3.5	195	22	3	220
Pasaia 61	2007-05-11	61	12	H	76	-39	9.6	480	211	125	816
Hondarribia	2007-01-25	42	8	H,F	20	169	1.8	379	94	18	491

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13 Recommendations and Action list

The actions and recommendations are listed in Annex 5.

14 Chair(s) for 2010

In 2008, Patrick Roose was appointed as Chair of the working group with Lucía Viñas as co-Chair in order to divide the workload. Given the fact that ICES EG chairmanship is a three-year term and both chairs are willing to continue, chairmanship should continue as it is for 2010–2011.

15 Date and venue of the next meeting

Craig was kind enough to invite the group to his institute Marine Scotland, Marine Laboratory, United Kingdom, for their 2011 meeting.

16 Closure of the meeting

The meeting was closed on Friday, 12 March 2010 at 13:30. Both Chairs thanked the group for their collaboration to a successful meeting and thanked, on behalf of the entire group, Maria J Belzunce and her colleagues for hosting the meeting in such an outstanding way.

Annex 1: List of participants

NAME	ADDRESS	PHONE/FAX	EMAIL
Maria J. Belzunce	AZTI Herrera kaia, Portuald z/g 20110 Pasaia (Gipuzkoa) Spain	TEL: +34 946 574000 FAX: +34 946 572555	jbelzunce@pas.azti.es
Ingemar Cato	Division of Geophysics and Marine Geology Geological Survey of Sweden (SGU) Box 670 SE-751 28 UPPSALA Sweden	TEL: +46 (0)18179188 FAX: +46(0)18179210	Ingemar.Cato@sgu.se
Kirsten Jørgensen	Marine Research Centre Finnish Environment Institute (SYKE) P.O.Box 140 FI-00251 Helsinki Finland	TEL: +358 400 148 599 FAX: +358 9 495913	kirsten.jorgensen@ymparisto.fi
Per Jonsson	Institute of Applied Environmental Science - ITM Stockholm University SE-106 91 Stockholm	TEL +46-8- 6747472	per.jonsson@itm.su.se
Claire Mason	Cefas Burnham-on- Crouch Laboratory Remembrance Avenue Burnham-on-Crouch Essex CM0 8HA United Kingdom	TEL +44 1621 787200 FAX +44 1621 784989	claire.mason@cefas.co.uk
Kristoffer Naes	Norwegian Institute for Water Research Southern Branch Televeien 3 N4879 Grimstad Norway	TEL +47 (37) 295067 FAX +47 (37) 044513	kristoffer.naes@niva.no
Koen Parmentier	Instituut voor Landbouw- en Visserij Onderzoek ILVO Visserij Ankerstraat 1 B-8400 Oostende	TEL+ 32(0)59 5698.57 TEL + 32(0)59 3422.50 FAX+ 32 (0)59 33.06.29	koen.parmentier@ilvo.vlaanderen.be

Johan Nyberg	Division of Geophysic and Marine Geology Geological Survey of Sweden (SGU) Box 670 SE-751 28 UPPSALA Sweden		Johan.nyberg@sgu.se
Craig Robinson	Marine Scotland Marine Laboratory P.O. Box 101 375 Victoria Road Aberdeen AB11 9DB United Kingdom	TEL: +44 1224 876544 FAX: +44 1224 295511	robinsonc@marlab.ac.uk
Patrick Roose (Chair)	MUMM 3de en 23ste Linierregimentsplein B-8400 Oostende Belgium	TEL +32 59 24 20 59 FAX: +32 59 70 49 35	p.roose@mumm.ac.be
Stefan Schmolke	Bundesamt für Seeschifffahrt und Hydrographie Wüstland 2 22589 Hamburg Germany	TEL: +49 40 31903330 FAX +49 40 31905033	stefan.schmolke@bsh.de
Foppe Smedes	Deltares Princetonlaan 6 PO. Box 85467 3508 AL Utrecht	TEL: +31 888662190 FAX: +31 30 256 4855 www.fsmedes.nl	foppe.smedes@deltares.nl
Céline Tixier	IFREMER – DCN/BE/CO rue de l'Île d'Yeu B.P. 21105 F-44311 Nantes Cédex 03 France	TEL:+33 2 40 374134 FAX:+33 2 40 374075	celine.tixier@ifremer.fr
Lucía Viñas (Co-Chair)	Inst. Español de Oceanografía Centro Oceanográfico de Vigo Cabo Estay – Canido Apdo 1552 E-36280 Vigo Spain	Tel: + 34 986 49 21 11 Fax: + 34 986 49 86 26	lucia.vinas@vi.ieo.es

Annex 2: Agenda

The 30th meeting of the ICES Working Group on Marine Sediments in relation to pollution, San Sebastian (Spain) 8–12 March 2010

Acting Chairs Patrick Roose and Lucia Viñas

Start at 8 March at 9:00 (all meeting days).

Closure of the meeting is foreseen at 17:00, 12 March

ITEM	ToR	SUBJECT
1	a)	Opening of the meeting,
	b)	Reflections on the changes in the ICES advisory and scientific process
2		Adoption of the agenda Arrangements for a working schedule and appointment of rapporteurs Recall actions and Recommendations Sediment Monitoring
3	a	Review and comment on the report of the 2009 meeting of OSPAR/MON in relation to sediments.
4	b	Review information relevant to the regionalisation of pivot values and background concentrations of contaminants in sediment.
5	c	To report on the uncertainty in data assessments arising from the selection of co-factors. Background concentrations
7	e	Continue collection of data and develop background concentrations for alkylated PAHs. Sediment dynamics
8	d	To develop plans for a further cooperative research report on the implications of sediment dynamics for the organisation and interpretation of sediment monitoring. Passive Sampling
9	f	Report ongoing and new projects involving passive sampling: Projects that combine biological effects measurements with passive sampling; National projects involving the use of passive samplers; International cooperative projects involving passive sampling, including the ICON project;
10	g	Undertake a review of partition coefficients for organic contaminants in sediments. Developments of monitoring guidelines
11	h	Finalise the technical annex to the JAMP Guidelines for monitoring of dioxins in sediments.
12	i	Finalise the technical annex to the JAMP Guidelines for monitoring of monitoring of PFOS in sediments.
13	j	Finalise the technical annex to the JAMP Guidelines for monitoring of chlorinated biphenyls in sediment. Sediment normalisation
	b	See agenda item 4.
14		Miscellaneous
15	k	provide expert knowledge and guidance to ICES Data Centre (possibly via sub-group) as requested

16	l	Report to SSGHIE on potential and current contributions of your EG to the Strategic Initiative on Coastal and Marine Spatial Planning (SICMSP).
17	m	Report to SSGHIE on your plans to promote cooperation between EGs covering similar scientific issues.
		Any other business
18		Recommendations and Action list
19		Chair(s) for 2011
20		Date and venue of the next meeting
21		Closure of the meeting
		Intended closure time is Friday 12 March at 17:00

Annex 3: Application of DGTs, mussels and TIE techniques for contaminant labile fraction evaluation, as an environmental assessment approach: an example in a Spanish Estuary

Natalia Montero, María Jesús Belzunce, Joxe Mikel Garmendia, Joana Larreta, Izaskun Zorita and Javier Franco

AZTI-Tecnalia, Marine Research Division, Herrera kaia, Portualdea z/g, 20110 Pasaia, Spain. Contact email: nmontero@azti.es

Introduction

Since the publication of the European Water Framework Directive (WFD; 2000/60/EC), efforts have been centered towards the compliance of the established Environmental Quality Standards (EQSs) in order to achieve the good chemical status. On the other hand, the WFD focuses on the biological and ecological elements of the ecosystem for the assessment of the quality of a water body. Therefore, it is essential to develop efficient monitoring methodologies to fill the gap between chemical analysis and toxicity upon organisms, in order to achieve a more representative picture of water quality.

In this study, water was evaluated by the use of Diffusive Gradient in Thin-Films (DGTs), since the labile metal species accumulated on these devices are more likely to represent the bioavailable fraction. Water chemical assessment was complemented with metal concentrations in mussel tissues, since both, DGTs and mussels, are representative of the time-integrated bioavailable metal in the water column.

Moreover, Toxicity Identification and Evaluation (TIE) procedures were carried out in whole sediments. Samples were physically/chemically manipulated to reduce the bioavailability of specific contaminants of the sample, in order to identify the chemicals responsible of toxicity. Efforts were centred on the three classes of contaminants that predominate in toxic sediments: ammonia, metals and organic compounds. Afterwards, toxicity reduction was proved by laboratory bioassays; 10-days acute survival tests with marine amphipods (*Corophium multisetosum*).

Material and methods

Historically, the Oiartzun estuary (North-eastern Spain) has been highly contaminated by the surrounding industries (thermal power station and paper mill) and by the shipyard activities. Four sampling-stations were chosen along the estuary following contaminants concentration gradient; three in the inner part of the estuary (P, L and H) and one in the outer part (C).

The monitoring schedule consisted in two sampling-times; May and June. Both, in May and June, three DGT probes were deployed at each station and retrieved after ten days. At the same time, mussels from a clean area were also transplanted, after 24 hours of depuration. One batch of mussels was retrieved after 10 days together with the DGT probes, and in order to study mussels bioaccumulation kinetics, another batch of mussels was left for a month. In June superficial sediments were also collected in all the stations, by a Van Veen grab. TIE techniques were applied to the sediment and toxicity reduction was proved by means of whole-sediment bioassays.

Results and Discussion

In Figure 1 has been collected the results regarding zinc accumulation in both DGTs and mussels. In May there were not significant differences between stations while in June, C station, which is located in the outer part of the estuary would be considered as the less impacted station. In mussels' case, no trend was perceptible. Moreover, a decrease in Zn concentration in mussels soft-tissues was observed from t10 to t30, which could lead to the overestimation or subestimation of metal concentration depending on the sampling-time.

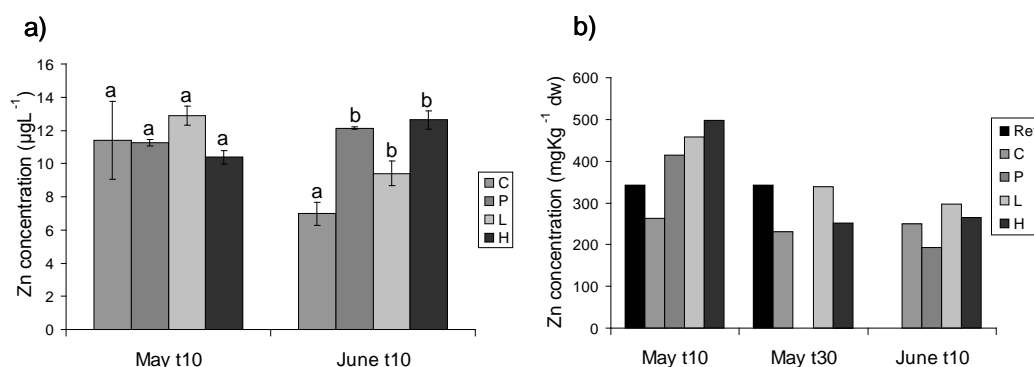


Figure 1. Zinc concentration measured by DGT (a) in the seawater ($\mu\text{g L}^{-1}$) and (b) in mussels soft-tissues ($\text{mg kg}^{-1} \text{ dw}$). a) DGTs May (t10) and June (t10) results are represented as mean \pm SE. Bars with the same letter are statistically equal (1-way ANOVA; LSD), b) Results in May (t10 and t30) and June (t10) of 20-pooled mussels. Key: Ref indicates background levels (pre-deployment).

In the case of lead (Figure 2), the opposite tendency was detected between DGTs and mussels. In order to explain this difference we regarded to the secchi disc values, which provides a qualitative value of suspended matter. We realized that with very low secchi values in May t10 (<1–1.5 metres) lead concentration in mussels soft-tissue was much higher than in pre-deployment conditions only ten days after the transplant. Afterwards, lead concentration decreased dramatically in tissues from May t10 to May t30, while secchi values were much higher (3–6 metres).

Moreover in June t10, with common secchi values for this area (1.7–4 metres) lead concentration in soft-tissues was similar to that in May t30. The outer station would be characterized as the cleanest by DGTs, as it occurred for Zn.

Regarding to this data we hypothesize that probably Pb was associated to particles in May t10, being accessible to mussels via active filter feeding but not to DGTs, and therefore they would be measuring different lead species.

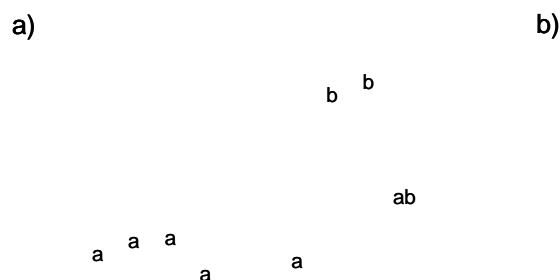


Figure 2. Lead concentration measured by DGT (a) in the seawater ($\mu\text{g L}^{-1}$) and (b) in mussels soft-tissues ($\text{mg kg}^{-1} \text{ dw}$). a) DGTs May (t10) and June (t10) results are represented as mean \pm SE. Bars with the same letter are statistically equal (1-way ANOVA; LSD), b) Results in May (t10 and t30) and June (t10) of 20-pooled mussels. Key: Ref indicates background levels (pre-deployment).

The data regarding whole-sediment bioassays are reported in Figure 3. Three samples resulted toxic when compared against the control (Figure 3a: P, L and H). These three sediments showed mortality values significantly different ($p < 0.05$) and 25% higher than in the control sediment. These three samples were treated by means of TIE techniques (Figure 3b). Three treatments were applied to each of the sediment samples and reduction on toxicity was assessed by comparison with the untreated sample, named baseline. In P and H stations the toxicity was reduced by the treatments applied to reduce the bioavailability of metallic and organic compounds. In the case of L, the organic compounds would be concluded to be the responsible of the observed toxicity.

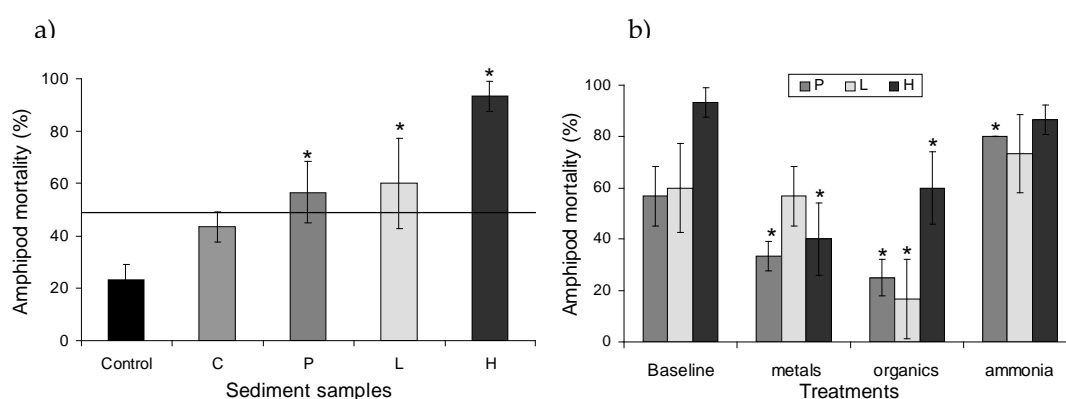


Figure 3. Amphipod mortality percentage after exposure to sediments and to whole-sediment TIE manipulations. a) amphipod mortality in unmanipulated samples in comparison with control sediment. The line indicates a 25% difference from the control mortality value b) TIE treatments applied to toxic sediments. * denotes a significant difference ($p < 0.05$).

Conclusions

A pollution gradient has been identified along the estuary by DGTs and TIE techniques, which have characterized the outer station as the less contaminated. However, based on mussels' results it would be difficult to discriminate between stations.

Interpreting mussels related data reveals difficulties due to the influence of abiotic and biotic factors in bioaccumulation. On the other hand, DGTs seem to be more reliable for representing metal distribution trends in highly variable water bodies. Differences in uptake between mussels and DGTs should be considered as species dependent different uptake. Moreover, the combination of biomonitors with DGTs allows for obtaining different and complementary types of information about metal bioavailability.

Based on the results obtained by DGTs and TIEs, it can be concluded that those techniques that account for the 'labile' fraction of toxicants are a more realistic approach to toxicity than dissolved concentrations demanded by guidelines.

Annex 4: Passive sampling in sediment, theory of uptake processes, variables and process control

Prepared by Foppe Smedes

Introduction

Passive sampling is practically entering a reference phase in an environmental compartment in order to measure the level of contaminants in that compartment from the sorption of contaminants by that reference phase. The driving force for uptake is the difference in chemical activity between the reference phase and the sampled medium. The uptake is always considered to be through the water phase and the mass transfer rate in passive sampling is generally controlled by the diffusion through the water boundary layer (WBL) and the polymer. Different materials are used as sorbing phase and are generally all some form of organic compound (lipid, cyclodextrine) or organic polymer (LDPE, PDMS, POM, different variation of styrene copolymers, etc.).

The copolymers are particulate materials with large uptake capacities that more or less sorb the concentration releasable to the water phase out of an environmental compartment, e.g., a sediment sample, but will never reach equilibrium. These materials (Tenax, xad, etc.) are mixed with the sediment and after some preset period separated from the sediment and analysed to estimate some level of released/available concentrations. Such methods are generally operationally defined.

This document focuses on polymer materials like LDPE, POM and PDMS used for the most common passive sampling approach that studies bioavailability of compounds in sediments based on the principle that the passive sampler is exposed to a sediment sample until equilibrium is obtained between the two phases. The partition theory says that in equilibrium the concentration of compound in the sampler is directly proportional to the freely dissolved concentration of sampled compounds in pore water (by the sampler - water partitioning coefficient, K_{pw}). Because this freely dissolved concentration is considered to be the driving force for transport or the uptake by aquatic organisms, it is also considered as a measure for the bioavailability. In equilibrium passive sampling sampler water partition coefficients (K_{pw}) are determined and when equilibrated with the sample medium the freely dissolved concentration in the water phase (C_w) can be estimated from the concentration analyte in the polymer sampler (C_p):

$$C_w = \frac{C_p}{K_{pw}} \quad (1)$$

Mechanistic considerations

Application of passive sampling (PS) may lead to uncertainties in cases where relevant mechanistic processes are ignored or not properly dealt with. The quality of PS-results may benefit by considering the following points:

- 1) To obtain a true equilibrium the internal diffusion in the sampler material should be proven sufficiently high not to limit the uptake;
- 2) Suspension density must be high enough to ensure sufficient transfer rate to the sampler;

- 3) The ratio of sediment to sampler capacity must be in such order that depletion of sediment is avoided or properly corrected for;
- 4) The analytical procedure that is involved in the method should preferably match the common procedures of (commercial) laboratories and allow cleanup;
- 5) Proper quality control on the processes that involve the passive sampling and ensure that equilibrium is obtained and the level of depletion is negligible.

These considerations are discussed below.

Diffusion and uptake of passive samplers

First a small mind jump. In passive sampling of sediments an amount of sediment (m_s) is equilibrated with a passive sampler (m_p). The initial process is that the sampler extracts the compounds from the pore water and the concentrations are restored by desorption from the sediment based on the organic-water partition coefficient of K_{oc} (L/kg). If m_s sediment is considered with an organic carbon content of f_{oc} then for a certain compound the sediment represents a volume of $m_s \cdot f_{oc} \cdot K_{oc}$ water (L). A passive sampler extracts from that imaginary water volume and the theory developed for passive sampling of the water phase (Huckins *et al.*, 2006) can also be applied to sediment suspensions. Two processes control the uptake:

- Diffusion of the analytes through a stagnant water boundary layer (WBL) at the surface of the sampler
- Diffusion inside the sampler material once the analyte is taken up at the surface.

The water sided mass transfer rate constant (k_w) for the WBL equals:

$$k_w = \frac{D_w}{\delta_w} (m s^{-1}) \quad (2)$$

Highest transfer is obtained if the diffusion coefficient (D_w) is higher and the water boundary layer (δ_w) is smaller. This is equal for the mass transfer rate constant in the sampler (δ_p = thickness of the sampler or half the thickness when exposed from two sides) but to combine both mass transfer rates constants for the WBL and the sampler to an overall mass transfer rate constant (k_o) the higher solubility of the passive sampling material needs to be taken into account. As $S_p/S_w=K_{pw}$ the mass transfere coefficient is given by:

$$k_p = \frac{K_{pw} D_p}{\delta_p} (m s^{-1}) \quad (3)$$

This leads to the equation for sampling rate (R_s) found in the passive sampling literature as described by Huckins *et al.* (2006):

$$R_s = k_o A = \frac{A}{\frac{1}{k_w} + \frac{1}{k_p K_{pw}}} = \frac{A}{\frac{\delta_w}{D_w} + \frac{\delta_p}{D_p K_{pw}}} \quad (4)$$

The equation combines the resistance to transport in both the water phase and the sampler where k_o is the overall mass transfer coefficient and A is a surface area of the sampler.

To obtain the highest sampling rates δ_w and δ_p should be as small as possible and A and $D_p.K_{pw}$ as large as possible. D_w is a compound property and cannot be influenced other than by changing the temperature. The flow rate or turbulence around the sampler determines δ_w , i.e. the shaking intensity in an exposure of a sampler to a sediment suspension. This shaking speed cannot unlimitedly be increased as the sediment will start wearing the sampler or be grinded itself. For water highest sampling rates under stirring conditions (100L for a sampler of 450cm² surface area) were reported by Booij *et al.* (2003) which would lead to a δ_w of 25µm for a compound with MW=200. Booij claims that the uptake was still under WBL control. This is supported by the work of Rusina *et al.* (2007) who determined diffusion coefficients in different materials used for passive sampling. This included several silicon rubbers (PDMS), EXACT polymer, LDPE and POM. Rusina showed that silicone rubbers have the lowest internal transport resistance and it is expected that uptake is always WBL controlled. For LDPE diffusion in the membrane could be limiting the uptake for low hydrophobic compounds (LogKow<4) depending on the actual thickness of the WBL. Highest diffusion coefficients were found for PDMS. SPMEs are generally coated with PDMS and uptake of SPME will generally be WBL controlled.

For POM Rusina only could report that that LogD were <-14, <-15, <-16 and <-16 (m²/s) for naphthalene, fluoranthene, benzo[a]pyrene and dibenzo(ah)anthracene respectively as the diffusion coefficients were too low to measure. These data are in agreement with Ahn *et al.* (2005) who estimated LogD_{pom} values of -14 and -14.5 for phenanthrene and pyrene respectively.

From Ahn *et al.* (2005) it can be estimated that internal equilibrium in 0.5 mm POM would require about 6–10 weeks for phenanthrene. TerLaak 2008 estimated equilibrium times that suggest that uptake of POM in an about 30 day's period will be dominated by surface sorption and diffusion to the internal part is limited. This could also explain why different water-sampler partition coefficients were found for POM of different thicknesses as reported by Cornelissen (2008). Although this low internal diffusion will complicate the modeling of the uptake process but nevertheless the uptake remains correlated to the concentration in the system although dependence on experimental conditions may be expected. One should be aware that the slow internal diffusion also is relevant when samplers are extracted as the time required to diffuse inside the material is also required to diffuse out.

Influence of suspension density

It is assumed that passive samplers in suspensions only absorb analytes from the dissolved phase. That means that uptake, as far not limited by membrane resistance, is WBL controlled. Nevertheless Booij *et al.* (2003a) observed with LDPE samplers in sediment suspensions a much higher R_s than expected from water only. Smedes 2010 investigated this aspect by recording uptake curves at equal sampler to sediment ratios (1:8) for different suspension dilutions. Figure 1 shows such curves for phenanthrene and benz[k]fluoranthene. Especially the right hand graph shows clearly that the uptake is much faster at a high suspension density. The higher uptake rate (first order uptake model) is directly proportional to the sediment content in the water phase as can be seen from Figure 2. The sediment content is responsible for the slope and the intercept represents the water only uptake. This is explained as the presence of sediment particles disrupt the WBL, or enter the WBL, but in both ways shorten

the (average) diffusion distance between the particle and the sampler resulting in an enhanced uptake. Likely the slope is also influenced by sediment properties as grain-size and organic matter content. Notice that phenanthrene obtained equilibrium while for benz[k]fluoranthene the uptake is still in the linear phase. The rate constants differ about a factor 30 what is about the difference in K_{pw} for phenanthrene and benz[k]fluoranthene in PDMS. (Smedes *et al.*, 2009). The rate constants are inversely related to the K_{ow} and consequently equilibrium takes longer if compounds are more hydrophobic. Decreasing rate constants can be explained from the uptake by the sampler and not limited by the release from the sediment. The amount of sediment was constant in this experiment while uptake increased with suspension density. The above described was investigated using PDMS samplers but as it is a water sided process it will also apply to other passive samplers, although may not be as pronounced if internal diffusion controls the uptake.

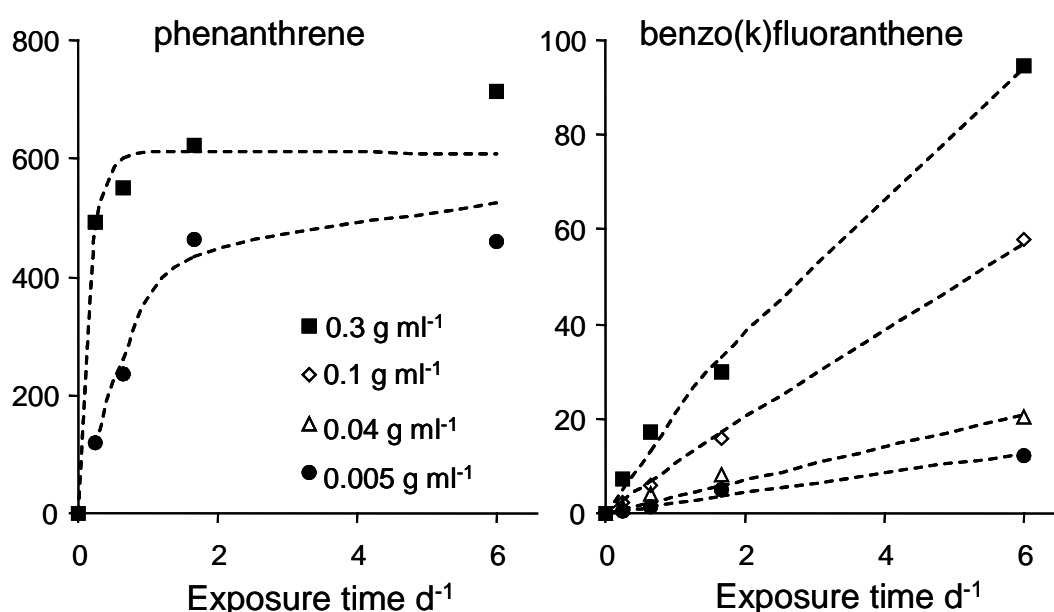


Figure 1. Uptake profiles of phenanthrene and benzo(k)fluoranthene for different sediment contents. Sampler to sediment ratio is 0.125 (constant for all dilutions). For phenanthrene only the curves for lowest and highest sediment content are plotted for clarity.

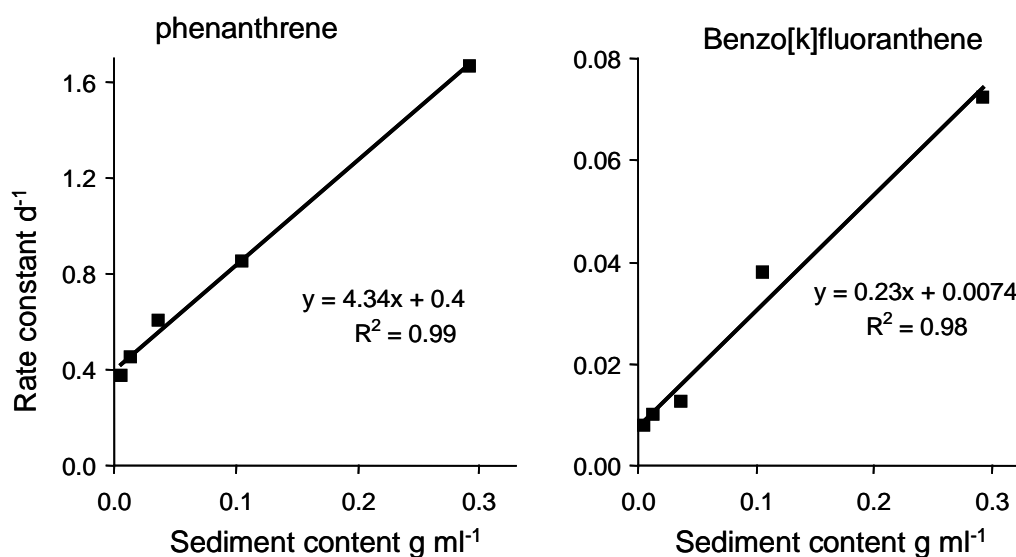


Figure 2. First order uptake rate constants relate to the sediment content in suspension.

Influence of sampler to sediment ratio

In first instance one would think that in a non-depletive sampling with a small sampler and a large amount of sediment equilibrium would be attained faster than the opposite situation where sediment will be depleted by the passive sampler. However the opposite is true. Figure 3 shows uptake curves for sampler to sediment ratios of 0.01, 0.1 and 1 for various compounds. For the highest phase ratio equilibrium is attained fastest. The clearest example is PCB 180 that reaches equilibrium at high phase ratio in a couple of days but at low phase ratio still is in the linear uptake phase after 48 days. Apparently the small amount of sediment is rapidly depleted in the presence of a large size sampler what results in fast equilibrium. In other words the depletion of the sediment assists in reaching equilibrium and processes meet somewhere in between. It is like two communicating vessels that obtain the same level faster if the level in the donor vessel decreases while the acceptor fills. At the other end, if the volume in the donor vessel is infinite large and the level is not affected the acceptor needs to be filled to the same level as the donor vessel what takes much longer.

Phase ratio and depletion in equilibrium passive sampling

To avoid that after equilibrium is obtained the amount taken up by the sampler has not significantly affected the initial concentration in the pore water it is crucial to select an appropriate capacity ratio between sample and sediment. An unaffected freely dissolved concentration of a contaminant in pore water can be determined when sampler's sorption capacity is kept well below that of the sediment sample to avoid depletion during the extraction. Above the capacity of the sediment in water volume was defined as $m_{s,foc} \cdot K_{oc}$ and likewise the capacity of the passive sampler equals $m_p \cdot K_{pw}$. If the water volume capacity of the sediment is far larger than that of the sediment, i.e. $m_p \cdot K_{pw} \ll m_{s,foc} \cdot K_{oc}$ the system will not be depleted by uptake of compounds through the passive sampler and the C_w calculated from the concentration in the sampler will closely resemble that of the original situation. If we assume $K_{pw} \approx K_{oc}$ for the amorphous carbon material a depletion of $\sim m_p / (m_{s,foc})$ can be expected. Clearly, the smaller the sampler the lower the change for depletion. In SPME where the sampler is very small depletion will also be expected small.

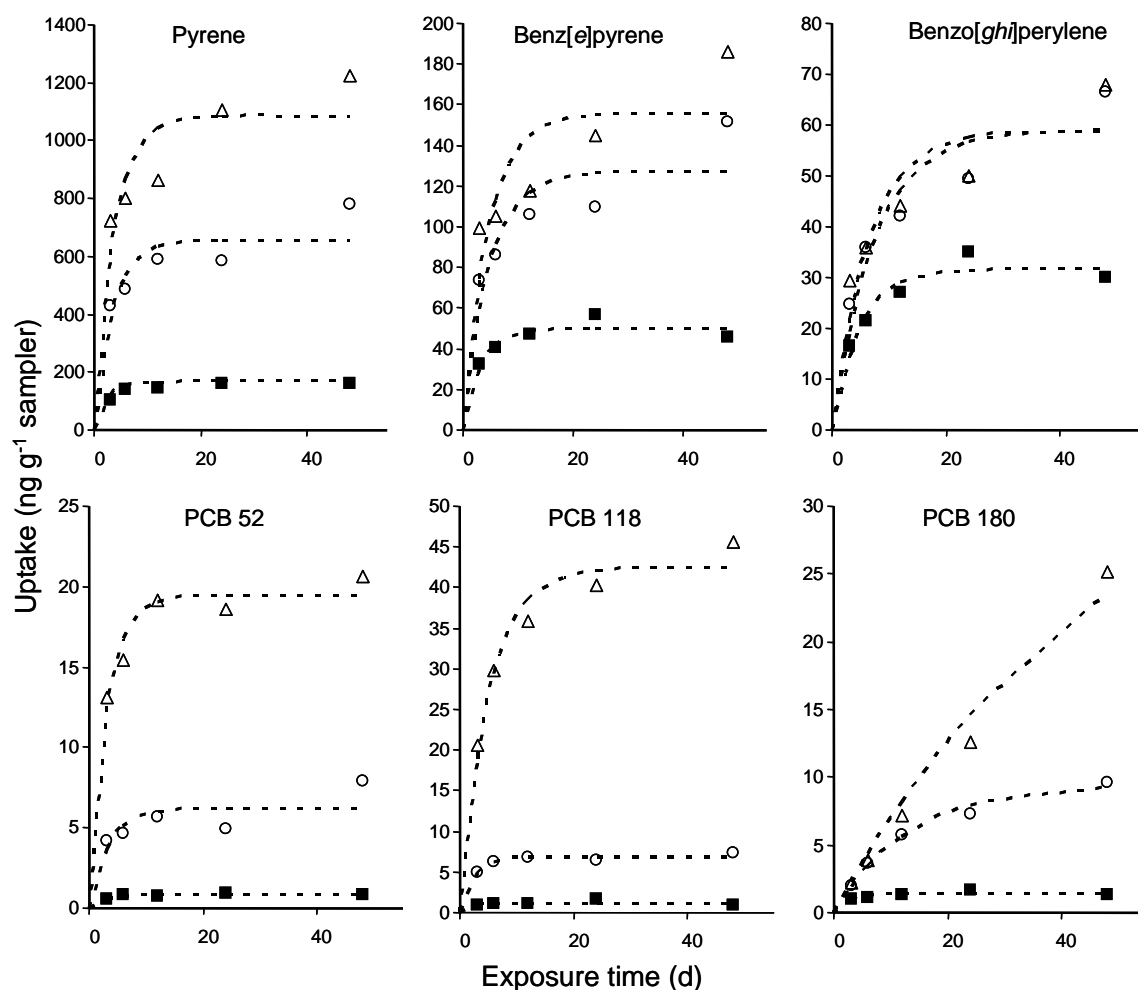


Figure 3. Uptake of passive sampler versus time for various compounds and different sampler-sediment phase ratios; 0.01 (Δ), 0.1 (\circ) and 1 (\blacksquare). Sediment content constant at 0.1 g mL^{-1} .

In Figure 3 the uptake is plotted as concentration in the sampler (equivalent to C_w) and the different equilibrium levels immediately reflect the effect of depletion on obtained free dissolved concentrations. The effect of phase ratio on depletion is compound dependent and cannot be fixed at a certain sampler to sediment ratio. Notice from pyrene to bens(ghi)perylene the difference between phase ratio 0.1 and 0.01 diminishes. Such a shift is not observed for the PCBs. This is the result of a different ratios between K_{oc} and K_{pw} values for different compounds that together with the sediment to sampler phase ratio determines the capacities of the individual phases. The figures are for PDMS rubbers that for similar K_{ow} values has relatively low K_{pw} values for higher PAHs opposite to PCBs. Secondly the K_{oc} of larger PAHs may be more higher than the K_{pw} compared to lower PAHs giving a higher capacity to the sediment resulting in lower depletions.

Correction for depletion

Reichenberg *et al.* (2008) confirmed a non-depletive situation by using increasing phase ratios showing them to have the same result. Smedes (2010) incorporated depletion in the passive sampling method and constructed sorption isotherms by exposing a range of different phase ratios. This allowed correction for depletion and at the same time an estimate of the accessible concentration was obtained. Figure 4 shows the result of multi phase ratio exposures. On the y-axis the C_w after exposure is plot-

ted and on the x-axis the residual concentration in the sediment after the equilibration. The right hand end of the graph is also the concentration in the sediment as determined by soxhlet extraction. The undepleted freely dissolved concentration (C_w^0) can be obtained by extrapolation to the y-axis. Note that the criterium allowing 5% depletion of the sediment (Mayer et 2000) is insufficient to guarantee negligible-depletion as for fluoranthene a 5% depletion of the total concentration gave a 20% lower C_w and for indeno(123-cd)pyrene about 5 times lower C_w would be obtained after 5% was extracted. In this example a sampler to sediment phase ratio of 1:100 already caused a decrease of over 30% of the freely dissolved concentration. Results from single point equilibrations that do not provide information on the level of depletion therefore should be considered with care as they may have underestimated the C_w in the original situation especially when sampler to sediment ratios are small.

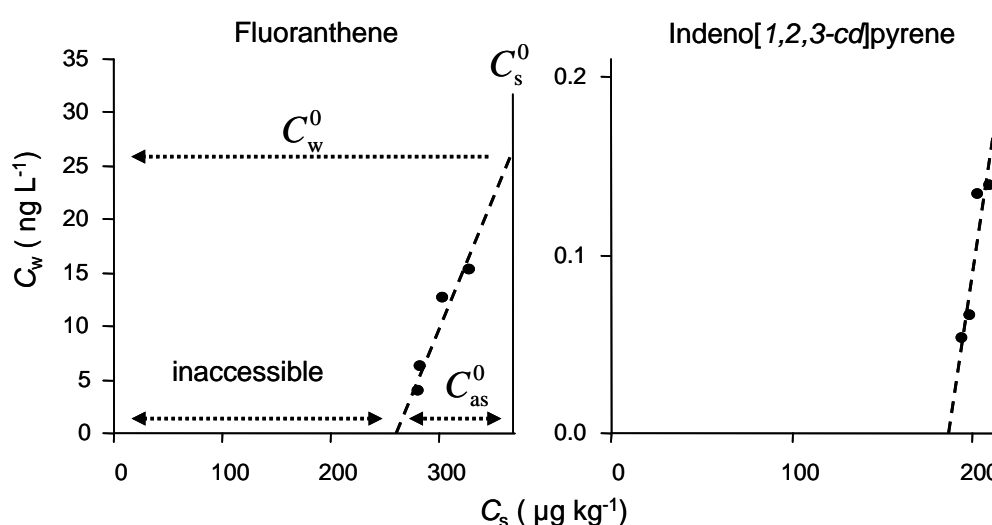


Figure 4. C_w plotted versus the (residual) C_s , actually representing a part of the sorption isotherm. The righthand y-axis is drawn at the concentration as determined after soxhlet extraction. (C_s^0) (Smedes, 2010).

Taking advantage of depletion

Depletion can also be used to estimate accessibility of analytes. While a small capacity sampler aims for a concentration in the pore water, a large sampler sediment ratio extracting the sediment exhaustively may give the concentration that is maximally released from the sediment. The contaminants remaining in the sediment following such extraction can be considered effectively unavailable. Basically this is measuring the both sides of bioavailability as conceptualized by Reichenberg and Mayer (2006). One is side is “chemical activity” that is basically proportional to the freely dissolved concentration ($\alpha \sim C_w/S_w$) and the second “accessibility”; the concentration in the sediment that can be released to the aqueous phase.

An estimate for the accessible concentration (C_{a0}) is provided by extrapolation to the x-axis as shown in Figure 4. Obviously, the isotherm will not go to zero but will likely move towards the origin at some point. Note that the slope of the line equals $1/K_D$ and a line with a low slope bending to the origin represents extreme high sorption. The time factor of these experiments is not very long but the results of the high sampler to sediment phase ratio in Figure 3, showing no increased release when shaking 48 days compared to ~4 days indicates that release from the inaccessible portion is at

minimum considerably slow. Using a range of sampler to sediment ratios a sediment-water partition coefficient for the accessible pool can be calculated by $K_D = C_{as}/C_w$ (reciprocal slope of the line in Figure 4) and subsequently $K_{oc} = K_D/f_{oc}$.

Process quality assurance

The approaches and processes considered above apply to different types of equilibrium samplers, but also the considerations made at the start of this document. Depending on sampler characteristics (e.g. surface area and volume) exposure conditions, etc., equilibrium may not be established for the most hydrophobic compounds during exposure and therefore the use of performance reference compounds (PRCs, such as used for surface water deployments, Booij *et al.*, 1998) can be used to quantify sampler-pore water exchange kinetics. The procedure for spiking passive samplers is described by Booij *et al.*, 2002. PRCs can, next to the verification of equilibrium, also be used to monitor possible depletion. PRCs distribute according to the sorption capacity ratio of sampler and sediment like the targets analytes do. If the capacity of the sampler is insignificant compared to that of the amount of sediment the PRCs will release completely from the sampler. Incomplete release from samplers indicates either incomplete equilibrium or depletion of the sediment phase (Smedes, 2007, and Smedes *et al.*, 2007b, 2007c). Since the rate of uptake and release are related to the hydrophobicity a residue of high hydrophobic PRCs on the sampler while the low hydrophobic are released (to a larger extend) indicates that equilibrium is not obtained for all compounds.

In case of exposures of multi sampler to sediment ratios PRCs will obviously remain in the sampler for situations where the sediment is largely depleted. In the presence of large amounts of sediment the PRCs will entirely be sorbed by the sediment. From the distribution of the PRCs between sampler and sediment a sorption isotherm can be constructed and from the slope *in situ* partition coefficients can be determined similar to native compounds.

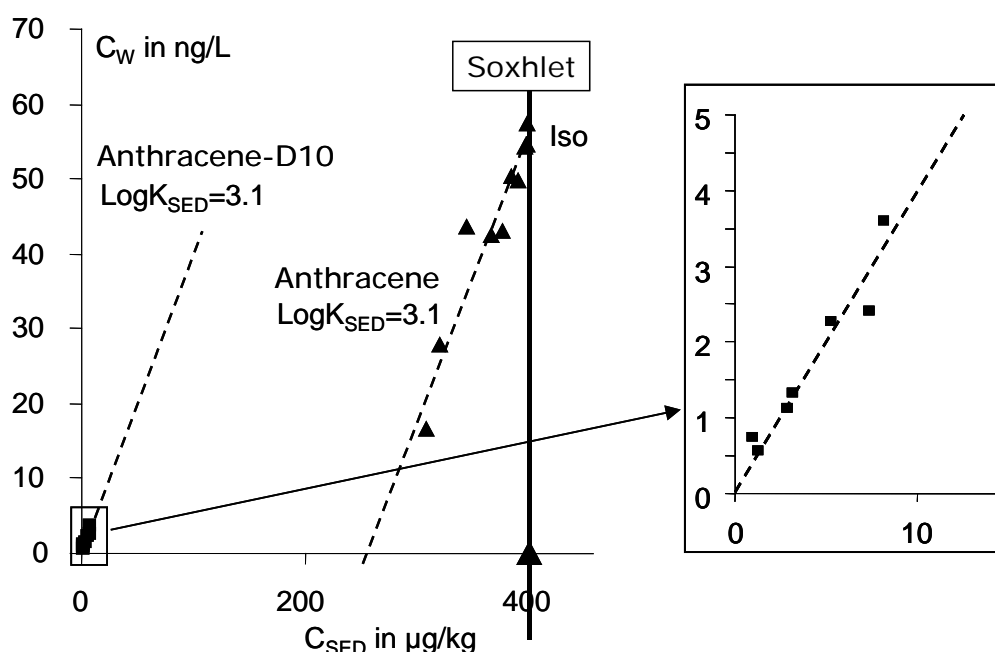


Figure 5. Sorption isotherms of Anthracene and Anthracene-D10 (added) in sediment from sludge depot IJsseloog. On the x-axis the concentration in the sediment (residual after exposure) is plotted and on the y-axis the freely dissolved concentration calculated from the concentration in the PDMS. In the right-hand graph the area around the origin is amplified.

Figure 5 shows the results of multi phase ratio exposures where also PRCs were added (taken from Smedes, 2007). The graph showed that added anthracene-D10 had an equal K_D as natively present anthracene. The difference is that the sorption isotherm of the natively present anthracene does not go through the origin while the added anthracene-D10 does. Apparently added compounds do not enter the inaccessible pool. Figure 5 also makes clear that with an individual exposure a K_{oc} is very much depending on the phase ratio selected. Applying the procedure used for single point exposures an isotherm through origin is assumed and for each individual phase ratio a different K_{oc} would be found. In literature K_{oc} values are generally a result from a single phase ratio and for a comparison more insight in the effect of the operational conditions is required. Largely shifted isotherms for native compared to spiked compounds are generally observed for PAHs but isotherms for PCBs are frequently equal for native and spiked compounds.

Concluding remarks

Mechanistic parameters in passive sampling were investigated for silicone rubber but likely apply to other sampling as well as it is a water sided process. Uptake rates are affected by the sediment content in suspension and faster uptake is obtained in dense suspensions. High sampler to water ratios give a faster equilibrium but this goes together with depletion and the obtained porewater concentration will often be an underestimation compared to the original situation. Correction by extrapolation is not straight forward as sorption isotherms are not necessarily linear from the origin. So to achieve an undepleted equilibration a large amount of sediment is required. A rule of thumb for a safe criterium could be that the sampler weight should be less than 10% of the amount of organic carbon in the system but this depends on the ratio of K_{pw} with the K_{oc} . Quality control on the process is very well possible by addition of performance reference compounds to the sampler.

Chances for depletion are less for small samplers like SPME. However for some groups of compounds cleanup will be necessary what is not easily performed with SPME.

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Annex 5: WGMS Terms of Reference 2011

The **Working Group on Marine Sediments in Relation to Pollution** [WGMS] (Chair: P. Roose, Belgium and L. Viñas, Spain) will meet in Aberdeen, UK in March 2011 to:

Sediments monitoring

- a) Review and comment on the report of the 2010 meeting of OSPAR/MON in relation to sediments.
- b) Review information relevant to the regionalisation of pivot values and background concentrations of contaminants in sediment.
- c) To continue work on the uncertainty in data assessments arising from the selection of co-factors.

Background concentrations

- d) Continue collection of data and develop background concentrations for alkylated PAHs.

Passive Sampling

- e) Provide a document discussing the different passive samplers presently used.
- f) To continue the work on passive sampling as a proxy for partition coefficients for organic contaminants in sediments
- g) Report ongoing and new projects involving passive sampling:
 - i) Projects that combine biological effects measurements with passive sampling;
 - ii) National projects involving the use of passive samplers;
 - iii) International cooperative projects involving passive sampling, including the ICON project;

Miscellaneous

- h) Provide expert knowledge and guidance to ICES Data Centre (possibly via sub-group) as requested

WGMS will report by DATE 2010 (via SSGHIE) for the attention of SCICOM and ACOM.

Supporting Information

Priority:	This Group handles key issues regarding monitoring and assessment of contaminants in sediments.
Scientific justification and relation to action plan:	<ul style="list-style-type: none"> a) Anticipating that the report of the proposed 2010 assessment will be available before the meeting, WGMS can review and comment the progress made; b) Background values and pivot values play an important role in the OSPAR assessments of contaminants in sediments. The regional character of both has thus far not been considered fully. WGMS will review any relevant information for regionalisation of both and advise accordingly. c) The uncertainty associated with the use of co-factors has potentially a significant impact on data assessments. WGMS will investigate this and advise accordingly. d) WGMS has proposed background concentrations on available information. However, the amount of available data is sparse. Additional information is expected and may warrant revision of the proposed background concentrations (OSPAR request 3, 2007) e) Passive samplers are increasingly used in environmental monitoring, but the approaches and methodologies differ. A document is being prepared inter-sessionally, discussing the different passive samplers, and is expected to be presented at the next meeting. f) Partition coefficients are used as a normaliser for organic contaminants by OSPAR MON. However, sediment sorption cannot always be adequately represented by the K_{oc}. WGMS will further investigate the use of passive samplers as an alternative. g) Receiving and review of national reports of projects involving the use of passive samplers by WGMS will build further experience on the field and use of passive sampling. Review by WGMS will contribute to the ICON objectives. h) Response to internal ICES requests.
Resource requirements:	None required
Participants:	The Group is normally attended by some 20 members and guests.
Secretariat facilities:	None.
Financial:	No financial implications.
Linkages to advisory committees:	ACOM
Linkages to other committees or groups:	WGBEC, MCWG
Linkages to other organizations:	OSPAR, HELCOM

Annex 6: Recommendations

RECOMMENDATION	FOR FOLLOW UP BY:
1. WGMS recommends that the existing approach to normalization and pivot point values should continue to be used in assessments, pending their continued work on this topic	OSPAR
2. WGMS recommends that additional data be used to further the work on normalisation and that a statistician with expertise in this area is asked to develop a statistical tool that allows a robust evaluation of whether differing pivot point values are required for differing regions, or sub-regions.	ACOM, OSPAR
3. WGMS recognises the value of passive samplers for sediment monitoring and deems the technique ready for application in the field. WGMS recommends that, whenever possible, passive samplers are used for trial sediment monitoring in parallel with the classical approaches.	ACOM, SCICOM
4. WGMS recommends that the 2007 guideline on passive sampling is published as an ICES TIMES series paper.	ICES
5. WGMS recommends that the technical annex for dioxins in sediments will be suitable for submission to OSPAR after their comments have been taken into account.	ACOM, OSPAR
6. WGMS recommends that, with the inclusion of their comments, the paper on the analysis of fluorinated compounds in marine matrices is fit for publication as an ICES TIMES series paper.	ICES

Annex 7: Action list

AGENDA ITEM	ACTION	WHO
4	Contact Rob Fryer and inquire if he is able to join next year's meeting and/or provide input for the normalisation discussions.	Craig Robinson
4	All members of the group are encouraged to submit data series that will support the work on normalisation.	All members
4	After consultation with Rob Fryer, make arrangements to present the procedure and outcome of the normalisation process during the MON assessments.	Foppe Smedes and Patrick Roose
4	WGMS members are invited to provide information in relation to pivot points and background concentrations, to allow further work on this issue next year.	All members
7	Provide new data on background concentrations of alkylated PAHs from the Mediterranean, Scotland and other relevant regions.	Céline Tixier, Craig Robinson and all members
7	WGMS members are encouraged to bring new information on background concentrations of alkylated PAHs to the meeting.	All members
9	WGMS members are encouraged to bring new information related to the use of passive samplers in environmental monitoring, particularly related to sediments.	All members
9	Make arrangements for a document discussing the application of different passive samplers in sediment monitoring. WGMS members will support Foppe in this task.	Foppe Smedes and all members
9 and 17	Contact the chairs of WGBEC and MCWG to investigate collaboration on the use of passive samplers in the marine environment.	The Chairs of WGMS
AoB	Forward the comments of their group to the chair of the working group that developed the CMA guideline for sediment and biota monitoring.	The Chairs of WGMS

Annex 8: Technical minutes of the Review Group MON1 2010

Review Group

Jarle Klungsøyr (Chair), Jacob de Boer, Michiel Kotterman, Colin O'Dowd*, Pia Andersson*

*Not present at the meeting

Introduction

RGMON1 worked by correspondence and met at ICES in Copenhagen May 3th 2010 to review the work done by four ICES working groups answering requests by OSPAR on:

- 1) Monitoring methodologies for ocean acidification (2010/2)
- 2) Atmospheric monitoring of PFOS (2010/6)
- 3) Tools for coordinated monitoring of dioxins, planar CBs and PFOS (2008/6, 2010/6)

Expert Groups Reports

Marine Chemistry Working Group Report 2010 (MCWG2010)

Working Group on Marine Sediments in Relation to Pollution (WGMS2010)

Working Group on Deep Water Ecology Report 2010 (WGDEC2010)

Working Group on Zooplankton Ecology Report 2010 (WGZE2010)

2008/4. Tools for coordinated monitoring of dioxins, planar CBs and PFOS

OSPAR Request

To prepare the following tools to support the coordinated monitoring of dioxins, planar CBs and PFOS under the OSPAR CEMP:

- a) technical annexes to the JAMP Guidelines for monitoring Contaminants in Sediments (OSPAR agreement 2002-16) and JAMP Guidelines for monitoring Contaminants in Biota (OSPAR agreement 1992-2) according to the structure of the existing technical annexes covering the following:
 - i) monitoring of dioxins in biota in sediments, taking into account advice from SIME 2007 that monitoring of dioxins in sediments should only be carried out in specific areas (such as sedimentation areas or estuaries) because of time lag (10–12 years) in deposition of quantities required for sampling;
 - ii) monitoring of PFOS in sediments, biota and water;
- b) to review the existing technical annexes on monitoring of chlorinated biphenyls in biota and sediment and propose revisions so that they are adequate for monitoring of planar CBs in these compartments, taking into account advice from SIME that monitoring in sediments should be undertaken only if levels of marker PCBs are e.g. 100 times higher than the BACs

and that for biota monitoring of concentrations in seabird eggs could provide an alternative matrix;

c) to develop background concentrations for dioxins.

RG Comments

Most of the questions in this request have been addressed previous years. The remaining issues are reflected in ToRs for MCWG2010 (c) Finalize technical annex for monitoring PCDD/Fs and “dioxin like” PCBs in sediments (with WGMS).

a (i) *Monitoring of dl-PCB and PCDD/Fs in sediments*

The draft guidelines for monitoring of polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs) and dioxin-like PCBs (dl-PCBs) in sediment give an updated overview of requirements and possibilities for PCB and PCDD/F analysis in sediment. This is useful, as many developments in technologies have taken place in this field. The document includes a lot of useful information and it may well serve to guide marine laboratories for analysing dl-PCBs and PCDD/Fs in sediments.

The guideline prepared is of good quality. The RG has some general and some more specific comments which are listed below.

According to SIME (2007) monitoring of dl-PCBs and PCDD/Fs in sediments should take place in specific areas such as sedimentation areas and estuaries. Monitoring dl-PCBs and PCDD/Fs in sediments differs from that in biota because other PCDD/Fs are present in sediment, in addition to the 2,3,7,8-substituted PCDD/Fs that are found in biota. Therefore, more selectivity is needed for sediment analysis. In contrast to biota, the PCDD/F levels – certainly in sedimentation areas – are normally higher. Consequently, the requirements for sensitivity are less stringent for sediments than for biota monitoring. This implies that laboratories do not necessarily need high-resolution mass spectrometry (HRMS). Low-resolution (LR) MS will probably do in most cases. The guidelines should mention this upfront, so laboratories should not be directed to investments which are not essential.

Recently, there has been a substantial development in bench-top mass spectrometers. Not only have LRMS instruments become more sensitive, but new types of mass spectrometers have entered the market. These instruments, Time-of-Flight (ToF) MS and Orbitrap MS fill a gap between LR and HRMS. Often they offer an even higher resolution than HRMS instruments. Orbitrap machines offer a resolution of up to 100 000. This resolution is, however, mass dependent in contrast to HR sector instruments, which normally offer a resolution of 10 000 or more, independent of the mass. A resolution of 10 000 (measured at 10% of the peak height) is needed for a proper dioxin analysis. To compare the resolution of HRMS sector instruments and that of ToF and Orbitrap instruments, the resolution of the latter two should be reduced by ca. a factor 2, as they are measured at 50% peak height. The guidelines should mention the options that ToF and Orbitrap MS offer. They require much less investment than a sector instrument does, while certainly for PCDD/F monitoring in sediments they will offer enough sensitivity and selectivity (full-scan options and high resolution). For more in-depth, academic studies, sector instruments may still be the optimum choice, but they are no doubt much more expensive.

The guidelines should also mention comprehensive-multi-dimensional gas chromatography (GCxGC) as a new technique for dl-PCBs and PCDD/F analysis. For dl-PCBs and PCDD/Fs in sediments GCxGC can even be used in combination with ECD, as this will offer enough sensitivity, and selectivity is much better than on single-

column GC provided a proper orthogonal combination of columns is selected. GCxGC can, however, also be used in combination with LRMS and, even better, in combination with ToF-MS as the latter offers a rapid response, which is ideal for the narrow peaks that come out of GCxGC.

New stationary phases have entered the market, such as liquid crystalline phases and ionic liquids. These are particularly useful to combine with e.g. non-polar columns in GCxGC to achieve sufficient orthogonality. The guidelines should mention polar that are often used in dioxin laboratories, and particularly for sediments, as more congeners are present than the 2,3,7,8-congeners that are present in biota. Table 4 should be extended as there is much more information on possible co-elutants of PCBs, e.g. in the papers of B. Larssen and S. Bøwadt from the 1990s. The section on temperature programmes is very limited. This should be extended. The 'solvent effect' is e.g. not mentioned at all. This is essential in the selection of the temperature program of the oven. Discrimination effects should also be mentioned.

Nowadays, standards for all dl-PCBs and PCDD/Fs, including all ^{13}C labelled compounds are available. Therefore, the Table 2 is actually redundant. One sentence in the text mentioning these standards are available is sufficient.

The description of the fractionation is very short. This should be improved because as it is now, the text does not give information on the proper order of columns to be used. It should be mentioned that a fat separation e.g. on alumina columns (or GPC but that is less efficient, even when more columns are used in series) is needed first. Then, a fractionation of PCBs, and OCPs is required on e.g. silica gel or Florisil. An extra cleaning step by sulphuric acid may be added (or the acid can be added to the silica column). Finally, the separation of the planar compounds (dl-PCBs and PCDD/Fs from the non-planar PCBs and other non-planar compounds) on a HPLC PYE or graphitized carbon column should take place. For the solvent reduction/evaporation steps the option of a Turbo-Vap should be mentioned.

The various additions should be made with reference to the appropriate literature. The paper can further be improved according to the suggestions given in Annex I.

b. Review guidelines for PCBs in sediments and biota to propose revisions to make them adequate for dl-PCB and PCDD/F monitoring

Monitoring planar (dl-) PCBs and PCDD/Fs in biota or sediments require specific guidelines. Guidelines for monitoring non-dl- ('regular') PCBs cannot be used for that. Guidelines for monitoring dl-PCBs and PCDD/Fs in biota have been prepared and are already accepted (ICES Advice report 2009, p.82-99). The guidelines for dl-PCB and PCDD/F monitoring in sediments have been discussed above under a.

c. Developing background concentrations for dioxins

PCDDs occur in nature, e.g. due to forest fires. Because these are also unintentionally produced by man, e.g. in waste incinerators, they are transported around the globe. Therefore, nowadays it is difficult to distinguish natural PCDDs from man-made PCDDs. The best option for finding background concentrations of PCDDs is to analyse sediment cores. The sediment layers that date back ca. 100 years ago should present background PCDD levels. MCWG in 2009 has tried to identify pristine areas, but these are difficult to find and little information is available (ICES MCWG Report Annex 17, p. 141). MSWG in 2009 has asked for additional work to collect data. It is suggested that MCWG may be asked to identify literature in which PCDD concentrations in deeper sediment layers (cores) are reported. A few useful papers could be added:

- Kjeller, L. O., and Rappe, C. 1995. Time trends in levels, patterns and profiles for polychlorinated dibenzo-p-dioxins, dibenzofuranes and polychlorinated biphenyls in a sediment core from the Baltic proper. *Environ. Sci. Technol.*, 29: 346–355.
- Alcock, R. E., and Jones, K. C. 1996. Dioxins in the environment: a review of trend data. *Environ. Sci. Technol.*, 30: 3133–3143.
- Czuczwa, J. M., Niessen, F., and Hites, R. 1985. Historical review of polychlorinated dibenzo-p-dioxins and dibenzfurans in Swiss lake sediments. *Chemosphere*, 14: 1175–1179.

Annex I: Detailed comments on Draft guidelines for monitoring dl-PCBs and PCDD/Fs in sediments

Title: Add " Guidelines formonitoring, etc.

Page 1

Line 3: Being... → As PCDD/Fs arestrongly

Line 6: Use abbreviation PCDD/F instead of chlorinated dioxin and furans in full

Line 8: add ref. (e.g. WHO, Van den Berg)

Line 15: Daelemans ref. refers to biota, better take ref. referring to sediments, and of more recent date.

Line 17: Neurotoxicity is a typical effect caused by ortho-PCBs but for non-ortho's?

Line 21: Spatial and temporal trend monitoring

Under Fig.1: Add paragraph with 'Objectives'

Analytes: 17 congeners: give arguments and ref. (WHO/EU)

3rd line: should be → are normally; ...dry matter and total organic carbon

4th line: last word: toxic → TCDD

5th line: However, although common practice ...

Page 2

Line 1: ICES guidelines: unclear: these ones or ref.?

Table 1: Give ref.

Sediments: PCDD/Fs, add: and dl-PCBs

Page 3

Line 2: add ref. on OSPAR JAMP guidelines

Page 3, 3 lines above Table 2: Give a better description of the way of spiking

Anal. Methods., line 5: state-of-the-art

Prep. Steps: Give quantitative indications of purities of solvents and reagents, rather than general statements like 'high purity'.

Cleaning: add enzymatic solution to remove fat rests, even for sediments

Baking: at which temperatures? Also: age of glassware is an issue: when scratched, then more active sites. Use new glassware from time-to time.

Last paragraph above Table 2, line 4: These internal standards are used to correct for errors and recovery losses.

Table 2 can be left out: just mention in text that ^{13}C standards are available for all target compounds

Page 4

Extraction, line 4: be consequent in use of abbreviations: PCDD/F, dl-PCB, HRMS

Line 5: add ref.

Last sentence: Provided the proper conditions are chosen, ...

Page 5

Line 3: mL

Line 9: recommended: replace by: essential clean up / clean-up? Be consequent in way of writing

Line 17: Ref. Van Leeuwen (2007) should be replaced by

Loco, J. van, S. van Leeuwen, P. Roos, S. Carbonelle, J. de Boer, L. Goeyens, H. Beernaert (2004). The international validation of bio and chemical screening methods for dioxins and dioxin-like PCBs: The DIFFERENCE project round 1 and 2. *Talanta* 63, 1169-1182.

Page 7

Add comments on software issues, on calibration curve problems (linearity or not).

Above table 7: Provide ref. for $\pm 15\%$

Page 8

Please give additional comments on problems with ion-suppression and need for extra clean up.

Page 9

Correction for blanks is not recommended.

Safety: do not use crystals for standards; do not analyse fly ash: if desired, an entirely new lab with specific safety precautions needs to be built.

Data reporting: add a comment on sieving of sediment with ref.