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19–23 March 2007

Hamburg, Germany

International Council for the Exploration of the Sea
Conseil International pour l'Exploration de la Mer

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Contents

Executive summary

Agenda item 3

OSPARMON made a preliminary assessment of the geographical distribution of ratios between contaminant (PAH, CB) concentrations. In some cases, an apparent change in ratios was observed to coincide with boundaries between data from different countries in the same general area (e.g. Southern Bight of the North Sea). These systematic differences were found to correlate with results from the QUASIMEME Laboratory Proficiency Schemes. This work will be elaborated further with a view on reporting the progress to OSPAR-MON 2007.

Agenda item 8

In 2006, a passive sampling trial field survey was initiated by WGMS and MCWG covering a survey at 31 stations from Portugal to Norway. A laboratory intercomparison was included through duplicate sampling and performing analyses by both the participating laboratories and by a central laboratory. The organisation of the trial ran according plan and is now at the stage of collating data from the participants.

The progress and initial results from the Passive Sampling Trial Survey (PSTS) were discussed together with the MCWG and are considered as a highlight of the meeting. The first field data show a great potential for the passive sampling methodology. Data confirmed known distributions of contaminants such as PAHs, CBs and HCB and also revealed gradients that were unexpectedly increased seawards (e.g. in the Scheldt estuary). The organisers hope to receive all data by May and will present further results at the ICES 2007 ASC Theme Session (J) on Passive Sampling.

Agenda items 8, 9, 10 and 11

The emerging methods and activities on passive sampling underline the potential of Passive sampling methods to address the bio-availability of contaminants is becoming more and more widely recognised

Agenda item 10

The group felt that the possible cooperation with the WGBEC members in the ICON project is a promising approach to linking passive sampling with biological effects measurements.

Agenda item 12

The excellent cooperation between WGMS and MCWG in 2006, when the two groups met simultaneously at ICES continued this year. Close communication between the two meetings enabled rapid and efficient exchanges of comments on the draft guidelines of brominated flame retardants and alkylated PAHs, and for progress of the documents towards a final form. However this is not yet completed and subgroup of WGMS and MCWG members will continue this work intersessionally.

Agenda item 13

Background values for alkylated PAHs in Sediment were proposed for trial use in assessment by OSPAR-MON. A subgroup will collect and process further data intersessionally with a view to reviewing the BCs next year.

Review Table

	Tor	Ag.	Summary of outcome	Communicate to:
a	OSPAR/MON sediments assessment. Ratios of contaminants in sediment.	3	WGMS reviewed the MON Annex 7 and attempted to correlate the outcome with QA data.	OSPAR MON
b,j	AMAP and Barents Sea	4,5	Two documents reviewed and advice offered to authors	AMAP, PINRO
g	Review the progress of the OSPAR One-off surveys, or, if already available, evaluate the data in collaboration with WGSAEM and MCWG	6	Reviewed progress and suggestions made for organisation of future programs	OSPAR/ICES
f	Continue the collection of information on different estuaries and case studies of the interpretation of monitoring data, taking into account sediment dynamics.	7	Plans for future work are made	
e	Evaluate intersessional activities on passive sampling methodologies; i.e.			
e	With MCWG evaluate PSTS for water and sediment including intercalibration,	8.1	Tremendous progress made showing strong potential for passive sampling methods	OSPAR
e	Small field trial on contamination by smelter discharges,	8.2	Field and experimental exercise was carried out jointly by NIVA and FRS. NIVA results presented.	
e	Other possibilities for international cooperation	8.3	Short review given of activities in Norway, Scotland, Belgium and France. Opportunities for national an international work included under 8.3	
h	to review and report on current state of knowledge of the use of passive samplers in sediment to address the activity of biologically active substances in the sediment, including both hydrophobic organic contaminants and other substances (e.g. metals)	9	Methods with great potential for the studies of sediment chemistry in relation to processes concerning nutrients and metals were discussed	
c	Review and report on the progress of cooperative work between WGBEC to WGMS on (bio)availability and related issues to report on opportunities for cooperative work	10	Suggestions are made to cooperate through the ICON project by including passive sampling in the core framework of ICON. Encouragement was expressed for various national projects.	WGBEC
d	Review the draft Guidelines on the use of passive samplers, to be prepared intersessionally by members of WGMS and MCWG	11	Guidelines were prepared but limited to the use of silicon rubber films. Practical usage is required prior to forwarding to OSPAR for adoption. Development of a dedicated website was proposed.	

	Tor	Ag.	Summary of outcome	Communicate to:
k	together with MCWG develop draft technical annexes on monitoring of polybrominated diphenyl ethers and hexabromocycladodecane in sediments following the structure of the existing technical annexes	12.1	In collaboration with the MCWG, the draft Technical Annexes were reviewed and amended. Those on PBDEs and HBCD are considered complete.	OSPAR
k	together with WGBEC and MCWG, review the existing technical annexes on PAHs and revise as appropriate to include alkylated PAHs	12.2	An intersessional joint WGMS/MCWG group formed to complete work on the PAH TA.	OSPAR when completed
	Develop proposals for background concentrations of alkylated PAHs in sediment: C1-, C2, C3-naphthalenes; C1-, C2, C3-phenanthrenes; dibenzothiophene and its Alkylated forms C1-, C2, C3	13	From a limited amount of data background values are proposed for trial use. More data will be collected from wider area to increases the basis of these values or adapt them when appropriate	OSPAR
i	Provide expert knowledge and guidance to ICES Data Centre on a continuous basis	14	Done as requested	
	Contributions for ASC 2007 Theme session J on Passive Sampling	15.1	Nine contributions were offered and a number of possible posters were noted	ICES
	External QA for passive sampling	15.2	WGMS welcomed the interest shown by QUASIMEME in developing LPS for passive sampling.	QUASIMEME
	Election of Chair	17	WGMS recommended that Foppe Smedes continues as Chair for one more year, with Patrick Roose as Co-Chair, with the view that Patrick Roose should take over as Chair after the 2008 meeting.	ICES

1 Opening of the meeting

The meeting was opened at 10:00 on 19 March 2007 by Stefan Schmolke on behalf of BSH and the sponsoring Ministries (Federal Ministry for the Environment, Nature Conservation and Nuclear Safety, and the Federal Ministry of Transport, Building and Urban Affairs). A further welcome was given the following morning by Prof Hartmut Nies, Head of the laboratory.

2 Adoption of the agenda

The agenda was adopted, with the addition to the AOB item of the organisation of Theme Session J for ICES ASC 2007, and contact with QUASIMEME.

The developments and activities following from the recommendations and action list from the 2006 meeting were reviewed. The outcome for the recommendations and actions list is included in Annex 4: and Annex 5: respectively.

3 Review and comment on the report of the data assessment from the 2006 meeting of OSPAR/MON in relation to sediments

This report relates to the assessment of sediment data at the 2006 meeting of OSPAR/MON. Due to insufficient additional data being available through ICES since the 2005/2006 assessment, no formal assessment of sediment data was done during the MON 2006 meeting. Difficulties were encountered in combining sediment data submitted in Environmental Reporting Format version 3.2 with data in 2.2 format, and this was the main reason why additional data for 2005 were not available for trend assessment. Therefore any assessment of sediment data could only cover data in 2.2 format and this would have been little different to that in the 2005/2006 CEMP assessment. MON decided not to prepare a complete assessment of sediment data but to carry out preparatory work on the spatial assessment of data for contaminants and contaminant ratios that had not been covered in 2005/2006 assessment. The results are summarised in Annex 7 “Evaluation of the feasibility and potential usefulness of assessing data on contaminant ratios in sediment” of the MON 2006 report.

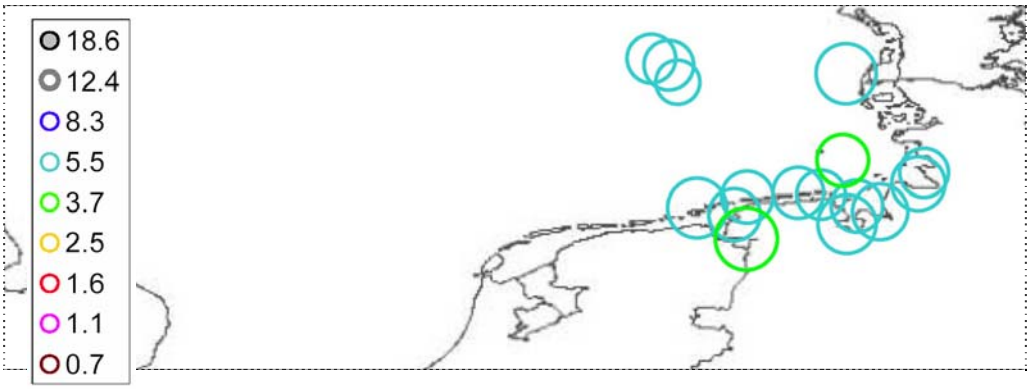
The annex presents certain concentration ratios of contaminants in sediment data. Ratios between selected PAHs and also between selected chlorinated biphenyls were viewed on a spatial basis. The aim was to explore whether contaminant ratios could be useful in differentiating between the contaminant burden from distinct sources. An attempt of the final interpretation was not made in the report. Processes such as differential rates of degradation and metabolism of components could also alter contaminant ratios. It was concluded that further investigations would be necessary to test usefulness of this approach.

A major advantage of analysing contaminant ratios was seen in the fact that no normalisation procedure is necessary to correct for varying composition of the matrix. No assessment was made about the uncertainty of the calculated ratios. Only data with reasonable high concentrations form the year 2000 or later were used.

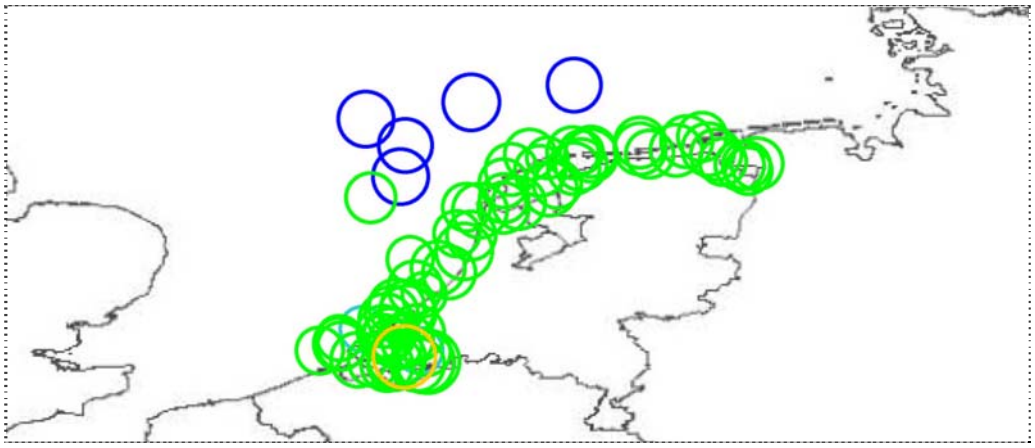
The ratios of Phenanthrene/Anthracene (PA/ANT), Fluoranthene/Pyrene (FLU/PYR), Fluranthene/Benzo[ghi]pyrene (FLU/BGHIP), CB153/CB118, CB153/CB28 were investigated. The PAH ratios are thought to have the potential to differentiate between pyrogenic and petrogenic sources. An increasing ratio of PA/ANT from the estuary to the open water was found in the western Scheldt and at the Swedish coast. Most low ratios were found close to the coast. FLU/PYR ratios showed little variation, and the inverse of the FLU/BGHIP ratio was in most cases in good agreement with the PA/ANT ratio. The

chlorinated biphenyl ratios CB153/CB118 also exhibit low variation with exceptions near Antwerpen, Scotland and Denmark. The ratio CB153/CB28 was not further interpreted due to large uncertainties of the CB28 measurement.

The regional comparison of the contaminant ratios in some cases revealed changes that corresponded with the geographical limits of national monitoring programs. E.g. PA/ANT ratio increases more or less in three steps along the coastline from the Western Scheldt to the German Bight (Figure 3.1). Systematic deviations between methods used in the national monitoring programs could be the reason for this.



Netherlands



Belgium

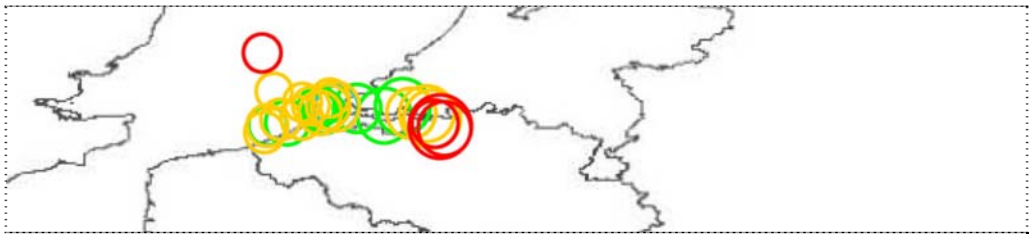


Figure 3.1. Ratios of PA/ANT for North Sea coast separated by reporting country.

A subgroup examined the spatial distribution of contaminant ratios with respect to systematic deviations in the measurement results corresponding to the geographical ranges of national monitoring programs. The investigation was based on Laboratory Performance Studies in the QUASIMEME Project since 2000, and these were compared to the contaminant ratios for field samples. The aim was to explore whether there are systematic deviations between measured contaminant concentrations (ratios) within identical QUASIMEME samples and whether this correlates with differences observed between national monitoring programs. Results from QUASIMEME Rounds R20, R22, R24, R26, R28, R30, R32, R36, R38, R40,

R42 and R44 were considered. For each Round and each Laboratory, the contaminant ratios were calculated. These ratios were normalised to the mean contaminant ratio calculated for each QUASIMEME round, i.e. equivalent samples. The normalised values could be used for the assessment of systematic deviations in the performance of national laboratories with respect to the contaminants under investigation. The computed values are shown in Figures 3.2 to 5 (left hand) in box and whisker plots. Each box integrates a descriptive statistic (min, max, upper-, lower quartile, median) of all normalised ratios since 2000, which were measured by each national monitoring program. The right hand figures are displaying the aggregated results of the field measurements implemented within the national monitoring programs between 2000 and 2005. All contaminant ratios are grouped by national programs. Due to the fact, that by far the major part of sediment measurements was done in coastal waters, it could be assumed that at least the inner quartile box if the box plots reflects the majority of observations within coastal waters. This could be seen easily if comparing the spatial distribution of observations with the aggregated data in the box plots. Figure 3.1 gives the spatial distribution of the PA/ANT ratio along the southern coastline of the North Sea. The elevated ratios in the Netherlands EEZ are obvious. They differ significantly from the observations close to the coastline. Due to the small number of open sea data points, the robust statistic shown in the box plots (Figure 3.2 (right)) is not influenced by them. In this example, the open sea data are marked as outlier (red cross) since they are more then 1.5 times the interquartile range out of the box.

Comparing the normalised ratios computed from the QUASIMEME samples (left hand figures) with the ratios observed under the national monitoring programs, some similarities become obvious. The reported normalised PA/ANT ratios are in a similar range, except Belgium, were significant lower ratios has been observed. The scatter of data points were in most cases similar, only the data from Norway and Denmark shows a slightly increased spread. On the other hand the ratios calculated from the field data (right hand figure) are increasing along the coast line from Belgium over Netherlands, Germany to Norway. The low values in Belgium are correlated with also low ratios measured in the QUASIMEME samples which could suggest that this effect might arise from systematic differences in the data from the national monitoring programs. Also, the elevated UK field data are correlated with high ratios measured in the QUASIMEME samples. The low field data in Denmark are not reflected by the QUASIMEME results. The lowest values were observed in the Skagerrak and Kattegat region and may be due to significant geochemical differences between Baltic and North Sea sediments.

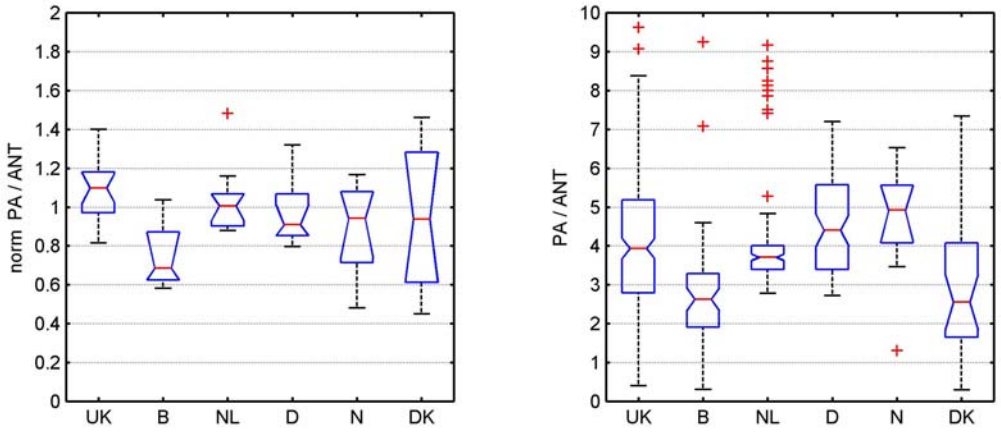


Figure 3.2. (left) Normalised Ratios of PA/ANT obtained for QASIMEME inter comparison experiments between 2000 and 2005. (right) PA/ANT ratios computed from field measurement results reported by the national monitoring programs during 2000 to 2005.

There were no significant deviations in the national FLU/PY measurements. The normalised ratios calculated from the QUASIMEME results also vary in a very narrow range only. The field measurements do not show significant regional changes.

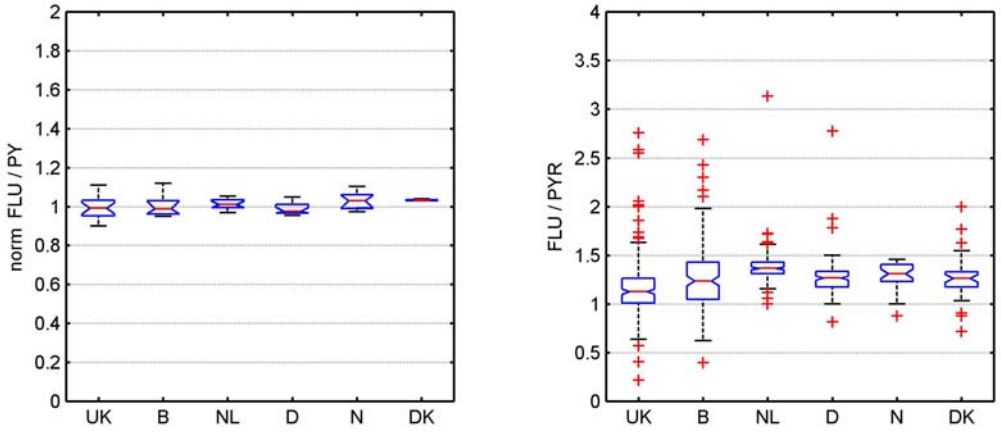


Figure 3.3. (left) Normalised Ratios of FLU/PY obtained for QASIMEME inter comparison experiments between 2000 and 2005. (right) FLU/PY ratios computed from field measurement results reported by the national monitoring programs during 2000 to 2005.

The FLU/BGHIP ratio observed in the field displays an opposite picture than the PA/ANT ratio. Low FLU/BGHIP ratios coincide with high PA/ANT ratios in Germany and Norway. But the general characteristic is also reflected by the QUASIMEME results, except the Norwegian values. The Norwegian field data are ending up in a low FLU/BGHIP ratio, the QUASIMEME results in an elevated ratio.

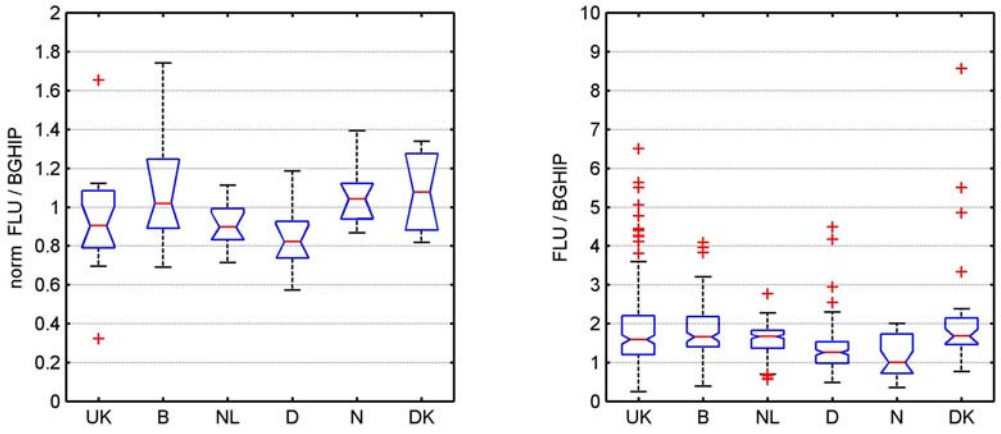


Figure 3.4. (left) Normalised Ratios of FLU/BGHIP obtained for QASIMEME inter comparison experiments between 2000 and 2005. (right) FLU/BGHIP ratios computed from field measurement results reported by the national monitoring programs during 2000 to 2005.

An almost constant increase of the CB153/CB118 ratios was observed in the field measurements around the North Sea. Lowest ratios in UK sediments and increasing values on the line from Belgium, Netherlands, Gemany to Denmark. Norwegian data were not available. The reference values from the QUASIMEME samples also show an increasing ratio from Belgium to Denmark; only the UK data do not fit in the same order which was observed in the field. At the current state of data evaluation, it is not clear to what extent the observed gradients in field samples are due to changing environmental concentrations (i.e. real effects) or whether they are only artificial effects arising from differences in laboratory analytical methods or sample handling and treatment.

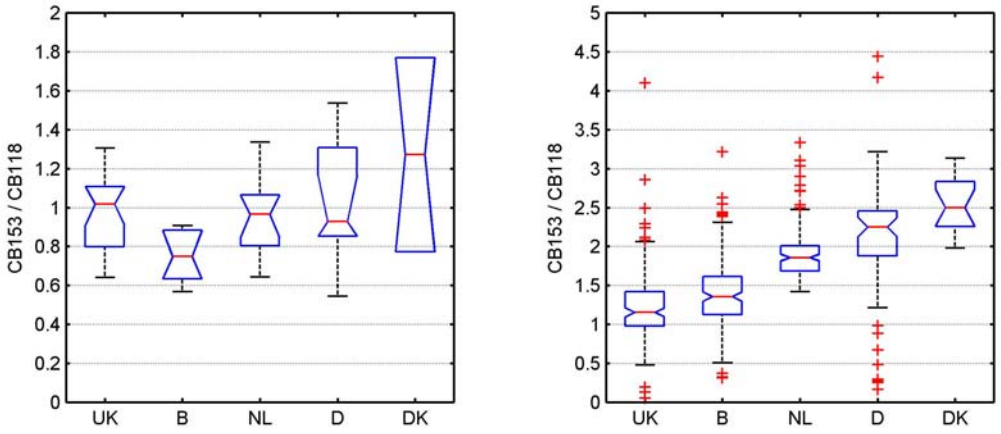


Figure 3.5. (left) Normalised Ratios of CB153/CB118 obtained for QASIMEME inter comparison experiments between 2000 and 2005. (right) CB153/CB118 ratios computed from field measurement results reported by the national monitoring programs during 2000 to 2005.

Conclusion

The group acknowledge the approach to utilise contaminant ratios as indicator for regional varying source patterns. Most promising are the PA/ANT and the FLU/BGHIP ratios. These ratios show, on one hand, distinct changes at distinct sites e.g. harbours. On the other hand, the inter comparability of different national monitoring programs seams to be reasonable. But further work has to be done on the evaluation of the measurement results compared to reference samples (e.g. QUASIMEME).

Also an additional effort should be put on the identification and evaluation of the most meaningful and reliable ratios. In particular, the ratios should be robust against deviations arising from analytical artifacts or alteration due to sample treatment and storage methods.

An estimation of uncertainty should be part of further data evaluation. A subgroup (organised by Stefan Schmolke) will continue intersessionally with a view to preparing a manuscript for possible submission to an appropriate journal.

4 Evaluate available information AMAP assessment and monitoring activities. Review of AMAP Assessment and Monitoring Activities

AMAP Assessments undertaken in 2002 (Heavy Metals in the Arctic and Persistent Organic Pollutants in the Arctic) were reviewed by a sub group in order to evaluate available information on the role of sediment chemistry in the AMAP assessment and monitoring activities including assessment criteria used. AMAP is an international organisation established in 1991 to implement components of the Arctic Environmental Protection Strategy (AEPS). Its objective is to:

"*Provide reliable and sufficient information on the status of, and threats to, the Arctic environment, and provide scientific advice on actions to be taken in order to support Arctic governments in their efforts to take remedial and preventive actions relating to contaminants*".

4.1 AMAP 2002 Heavy Metals and Persistent Organic Pollutants Assessments

There is limited data on sediments in these assessments, with the majority of the data relating to atmospheric inputs and measurements in biota. In the case of metals, the section of the report outlining Spatial Patterns (Chapter 4) makes reference to the fact that concentrations of trace metals in marine sediment depend on grain size, organic matter content, regional and local geology and proximity to local (including natural) inputs. It also states that surficial concentrations can also be affected by bioturbation and geochemical processes as well as ocean currents. But it does not appear to use any of these factors in the assessment of data. It states that for these reasons, MacDonald *et al*. (2000) concluded that marine sediments were not particularly good indicators of regional contamination and were inappropriate for examining spatial distributions.

Very little reference is made to sediment in relation to Temporal Trends, as there were insufficient data sets available. The assessment criteria used in assessing levels of contaminants was to compare with Effects-Range Low (ER-L) and Effects Range-Medium (ER-M) (Long *et al.*, 1995).

During the assessment of heavy metals, the report identified gaps in the knowledge obtained in the first assessment of 1998. This led to recommendation that heavy metal data collected for AMAP applications should be standardised for consistency in sampling, analysis, and reporting with a more comprehensive quality assurance/quality control protocol that will enhance intercomparisons of data sets. Data collected in Phase II added significantly to the general understanding of heavy metals in the Arctic but mainly in relation to atmospheric inputs and biota. For PCBs, OCPs and PAHs there is again limited data on sediments with the majority of the data relating to measurements in biota.

4.2 Conclusions

Reference is made to contaminant concentrations in marine sediment being dependent on grain size, organic matter content, regional and local geology and proximity to local (including natural) inputs, but these factors do not appear to be used in the assessments. The

small amounts of data presented are not corrected for grain size or organic carbon content. The 1998 assessment identified gaps in the knowledge obtained; however, these gaps are still apparent in the 2002 assessment.

Although AMAP consider sediments as inappropriate for examining spatial distributions, climate change in the Arctic region could result in changes in the amount and distribution of sea ice and land run-off. In turn, these may well lead to changes in the distribution and intensity of processes that sequester atmospheric contaminants in Arctic regions, and consequently alter the patterns of deposition of solid matter on the Arctic sea bed. Such changes involving both sediment supply and exchange processes with particles will make sediments monitoring important in the future.

WGMS suggest that sediments be considered in more detail in future assessments and that their interpretation could possibly be improved if AMAP adopts OSPAR MON Guidelines and assessment practices, and relevant OSPAR Technical Annexes. A representative of AMAP could attend MON 2007 to observe their assessment methods.

It was agreed the Chair to communicate the above with AMAP (Simon Wilson).

5 Developments in the assessment of sediment quality in the Barents Sea

WGMS received a report by Andrey Zhilin and Nataliya Plotitsyna from PINRO in relation to PAHs and OCs in the bottom sediments of the Barents Sea south of Spitsbergen. (see Annex 6). Further more a report of joint Norwegian/Russian report on "Monitoring of hazardous substances in the coastal areas of the Barents Sea: harmonisation with OSPAR's Joint Monitoring and Assessment Programme (JAMP). Experience from the pilot study 2002–2004" (SIME 07/6/Info.2-E), mainly focusing on coastal areas in Kola and Motovsky Bay areas.

5.1 PINRO assessment of 2005 sediment samples

The PINRO assessment consists of 26 sediment stations sampled in 2005, which have been analysed for grain size composition, PAH and OC. The methods used for the analysis are based on IOC guidelines for PAH (refluxed KOH/ethanol, spiking with 4 deuterated PAHs and GC-MS detection after filtration/extraction to hexane), and PCBs by GC after ultrasonic acetone-hexane extraction and purification with H_2SO_4 and Cu filings. The laboratory participates in QUASIMEME and uses IAEA-383 as a reference material. Quality Control is in line with OSPAR expectations.

There has been no attempt to normalise the data, but grain size distribution effects are considered and referred to, especially the Pelite (<63µm fraction of clay-silt). The Assessment is based on the sum of the 16 PAHs and Toxicological Equivalency Factors (TEFs) to calculate the total concentration of carcinogenic PAHs (CPAH), relying on the US-EPA interpretation of TEF of Benz(a)pyrene (BaP). The relative contents of BaPeqdose in TEQs are given, with Dibenzo(a,h)anthracene (DBA) contributing around 40% and BaP 30% in the samples.

Chemical fingerprinting of the PAHs is used in order to identify potential sources, using single compounds (Fluoranthene) and ratios (Phenanthrene/anthracene and Fluoranthene/pyrene) which are used to distinguish between pyrolytic origin (coal combustion) and diagenetic origin of the PAHs. It is concluded that shipping influences some areas where ratios indicates petrogenic origin at two stations, whereas the rest were characterised by pyrogenic PAHs, mainly attributed to coal combustion.

The OC's were within a range of a factor of 10 (in ng/g dry weight HCB 0.17–1.55, HCHs 0.27–2.26, DDTs 0.36–1.79 and PCBs 0.7–5.12), and except that the sum of PCBs was from 12 congeners, the main assessment was against other data from the Barents Sea region. For DDTs, the ratio of DDT/DDE was used to assess if there was local use of DDT. For PCBs the composition of low-chlorinated vs. high-chlorinated PCBs was used, with a predominantly low-chlorinated PCB content as indicative of atmospheric transport.

5.2 Russian-Norwegian 2002-2004 pilot study

This project is in accordance with JAMP guidelines and is a Norwegian-Russian collaborative project to extend OSPAR monitoring towards the west to the Murmansk coastline and Kola Peninsula, and also includes training of the Russian laboratories participating in the project.

The analysis is done in both sediment and biota. The coverage is 4 sediment stations, 5 blue mussel and 4 cod sampling stations. All in a gradient out from Murmansk and the Kola Bay.

The list of substances analysed is impressive, consisting of DDTs, chlordanes, toxaphenes, HCB, HCHs, PCBs, BDEs, dioxin/furans, PAH and heavy metals.

Assessment has been performed by using the Norwegian SFT classification system with classification of all compounds as Class I (slightly contaminated) or II (moderately contaminated) for Ni in all 4 samples, Pb and DDT/PAH/PCB in the Kola Bay area. A comparison of the results with Norwegian datasets from the North/west coast also indicates a low pollution load. TEQs have been used to evaluate the dioxins and sum of 7 PCBs, HCHs and HCB for the other chlorinated compounds.

For the biota sampling, stations closer to Murmansk and within the Kola Bay is included, and this gives an illustration of a declining trend from Murmansk into the open waters, except in the case of HCB, which was also found at high concentrations in the Pechanga Bay area. The worst case, when assessing using the SFT classification, is for DDTs in Kola Bay that is Class V (very strongly polluted), for the other stations and HCB/HCHs, only class II (moderately contaminated) is reached. PCBs are in class III to IV (markedly to strongly contaminated), also here Pechenga Bay is high. For PAHs moderately contamination is found for the sum of 16 EPA PAHs, but a large contribution of alkylated PAHs is noted.

PBDE was found in all samples, and assessment was made by EPA lowest observed adverse effect levels (LOAEL) of the PBDE group, suggested to be 1 mg/kg/day No dioxins, only furans was detected and TEQs were calculated but not assessed.

Heavy metals were found in the same range as OSPAR background values or around Russian normal levels, except Pb at Pechanga Bay that exceeded the Russian maximum permissible concentration (MPC value of 10 mg/kg wet weight).

For Cod, no results were above the Norwegian or Russian environmental or food quality criteria.

As a final remark, the project will continue and also include biomarkers.

5.3 Conclusion on assessments of the Barents Sea

i) The assessments were based on US EPA or Norwegian SFT assessment criteria, and for metals also OSPAR background values.

ii) The methods and quality assurance used are in line with the OSPAR requirements.

iii) The group remarked that outstanding work was done at PINRO and recommends to report the underlying data including cofactors to the ICES database so they can be included in OSPAR assessments.

iv) None of the reports use the normalisation guidelines. In the report obtained from PINRO a clear awareness and comment on the sediment grain size as a confounding factor was noted. Individual members of WGMS offered to assist PINRO with normalisation of their data. The chair will communicate this to PINRO (Andrey Zhilin).

6 Review the progress of the OSPAR One-off surveys, or, if already available, evaluate the data in collaboration with WGSAEM and MCWG

History: The OSPAR project for a One-off survey for endosulphan, SCCPs and 2,4,6 tri-tert-butylphenol in the marine environment has been underway in since 2004 (agreement 2004-14), and has been discussed in various OSPAR (MON, SIME, ASMO) and ICES (WGMS, WGSAEM, MCWG) working groups. Considerable time has been given to drafting details of a proposal for how and where to perform the one-off survey. This has led to a well-designed programme for the one-off surveys. To take the one-off surveys forward, a group of lead countries, Germany (endosulphan), Sweden (SCCP) and UK (2,4,6 tri-tert-butylphenol) agreed at SIME 2006 to work together to and produce a minimum programme with maximum response. UK offered to keep a sample bank on behalf of the contracting parties while waiting final financing.

The status of the One-off survey for endosulphan, SCCPs and 2,4,6 tri-tert-butylphenol was presented at SIME 2007. Sweden had sent out a questionnaire to the contracting parties on participation and containing a pricelist for the survey and analytical work, but had only received a reply from one contracting party. At the meeting, several contracting parties were not aware of this questionnaire, and it would be circulated again by the Secretariat to the contact points of SIME with an urgent request to reply, and if no data were available, to participate in the project. Even so, informally suggestions were that none of the contracting parties expected to be able to secure the funding – be it ever so small – for the survey, and to finish the survey in time for the QSR 2010, the samples should be taken and analysed no later than 2007.

It is the feeling of WGMS that the way this project had been taken forward was in principle sound, aiming at a one-lab solution and with a clear and agreed plan for sampling strategy, but the financial arrangement had failed. History has shown that the idea of a quick one-off survey to fill a gap of knowledge on a convention wide basis is not necessary easy to carry out, even if everybody agrees to the purpose and necessity of the survey.

WGMS suggest that a review of the funding arrangements for “one-off” surveys is needed. Possibly OSPAR/EU could hold a fund on behalf of Contracting Parties which could be used to contract one or a group of laboratories to carry out the work. The individual Contracting Parties would only have to supply samples and data in connection to the sampling. If the survey could be linked to their regular monitoring activities this should not be costly and might be feasible for contracting parties without too much extra effort.

An alternative to this approach would be for countries that are performing their own national screening or one-off surveys will open the survey for samples from other contracting parties to expand the geographical representation of the survey and in this way place their national results in a broader context.

7 Further work on collection of information on different estuaries and case studies of the interpretation of monitoring data, taking into account sediment dynamics

WGMS was asked to continue collecting information on sediment trend monitoring, taking into account sediment dynamics. The reason for the continuation of the work is that sediment dynamics, not only caused by natural processes but also by man-made changes of the marine environment, may significantly affect the concentrations of pollutants in sediments.

The group recognised that there is new information of importance from the Baltic Sea and Scheldt estuary that deserves to be included in the report on sediment dynamics.

Per Jonsson gave a short presentation of an investigation that aims at evaluating possible effects on the Baltic Sea sediments from climate change. A significant increase in sediment carbon content is likely to occur due to expected water level changes that will alter the present situation with a land-rise due to crustal rebound after the last glaciation of Scandinavia, into a water level rise in most parts of the Baltic. The under-lying factor is that the erosion/resuspension of minerogenic glacial and post-glacial clays, driven by the present land-rise, is likely to decrease substantially subsequently resulting in decreased bulk sedimentation. In parallel to the decreased supply of minerogenic matter, the riverine input of carbon and primary-produced carbon will constitute an increased portion of the sediment that in turn may affect the environmental fate of especially organic pollutants in the Baltic Sea.

A sub-group, consisting of Els Monteyne, Claire Mason and Per Jonsson discussed a recent paper by Fettweis *et al*. (2007) mainly dealing with mud origin, sediment characterisation in the Scheldt estuary and southern North Sea and possible links to human activities. One important conclusion that could be drawn from the paper is that deepening/widening of the navigational channel in the Scheldt estuary have significantly increased the input of "clean" suspended particle matter from the North Sea into the estuary. This strengthens the conclusion that already has been discussed in Annex 6: of the ICES WGMS Report 2005 (Sediment dynamics in relation to sediment trend monitoring), that these man-made changes may have substantial effects on sediment concentrations of pollutants in the estuaries.

The sub-group suggested to WGMS that the new information on the North Sea estuaries and the Baltic Sea at the next WGMS meeting which could result in a future revision of Annex 6 of the ICES WGMS Report 2005. Members are encouraged to supply any new information of importance of sediment dynamics for sediment monitoring.

8 Evaluate intersessional activities on passive sampling methodologies

8.1 Evaluate, with MCWG progress and outcome of passive sampling trial survey (PSTS) for water and sediment including intercalibration

8.1.1 Some introduction

A meeting of the Organising Group for the PSTS project had been held in BSH Hamburg on the Friday and Saturday immediately preceding WGMS 2007. The Group had been very encouraged by the progress of the project and with the results being obtained. A note of that meeting was presented to WGMS an MCWG, and is included as Annex 7: to this report.

8.1.2 Joint meeting with MCWG 21 March 2007

Kees Booij gave an introduction on passive sampling of compounds in water. He explained the uptake principles and the use of performance reference compounds to estimate the sampling rate. He concluded with a discussion on uncertainty and pitfalls.

Foppe Smedes delivered a presentation on the PSTS project to the joint meeting, covering the planning organisation of the project, the execution of the project, the data available to date and preliminary comments on the data.

During the presentation participants of Portugal were rewarded with a bottle of wine and congratulated with being the first Laboratory to send the results to the central laboratory.

Jacek Tronczynski commented that the project already appeared to have exceeded the initial objectives, and that the possibility to make comparisons between the results of passive sampling and the bioaccumulation of contaminants in mussels and worms is potentially of considerable benefit. These experiments expand on the original objectives. Patrick Roose expressed thanks to Foppe Smedes and other members of staff at RIKZ for the large effort they had put into making the survey a success.

There was some discussion of the advantages of having good measured values for the partition coefficients of the various analytes between water and the sampler as this directly influenced the estimates of sampling rate. Inappropriate values for the partition coefficients would result in poor estimates of the sampling rate and consequently of the dissolved concentrations of contaminants. It was noted that the model of sampling rates developed during the project was applicable in situations where the uptake was controlled by diffusion through the boundary layer around the sampler, but not for compounds of low K_{OW} where the membrane-transport can limit the uptake of contaminants. However, in such case equilibrium is often obtained making the sampling rate irrelevant.

There was a wide ranging discussion of the interpretation of the survey results, as a survey rather than as a technical trial or intercomparison exercise. It was noted that some aspects of the data were very reasonable and interpretable, for example the high concentrations of PAHs at some Norwegian stations close to aluminium smelters, and systematic changes in concentrations through the Scheldt estuary.

High concentrations of HCB in the Elbe were consistent with known sources of HCB to the more inland parts of the Elbe. High concentrations of PCBs in the Seine and the Scheldt were similarly consistent with known inputs.

The concentrations of some PAH in water in remote areas were unexpectedly high in comparison to those in inshore areas known to receive inputs of PAHs, and this information could have direct relevance to current discussions on Background Concentrations of these substances in biota.

It was noted that such a small amount of data should not be over-interpreted, or considered fully representative of coastal waters of the North Sea, and even less so of open waters. The lack of data for open waters was particularly noted.

There was some discussion of the concept of validation of passive sampling. The simplest way to think about the process is that it aims to determine the free dissolved concentrations of the hydrophobic compounds in water and pore water. The experimental work required to make an independent measurement of free dissolved concentrations is very difficult to carry out, and usually would still require the knowledge of a partition coefficient, for example between the free dissolved state and compounds associated with colloidal or dissolved organic matter. There could be considerable uncertainty in the values selected and in the outcome of the final comparison with passive sampler results.

A better way to consider passive sampling is that is reflects the activity of the substances in the water, and that this gives links to the activities of the substances in other phases such and sediment and biota. It is therefore reasonable to consider the relations between passive sampler results and residues in organisms at equilibrium, provided that the contaminants are not significantly degraded by the organisms. The environmental validation of the

measurements can be explored through comparison with bioaccumulation of contaminants by organisms.

8.1.3 The future

Firstly, it was agreed that Kees Booij should join the Coordinating Group for PSTS. The Group would work to gather the full data set for PSTS and to present conclusions at the Theme Session J at ICES ASC 2007 in Helsinki. Opportunities for external publication should also be sought.

There was some discussion of the way forward for this area of work. It was noted that some national initiatives were appearing (e.g. in Belgium, France and the UK) and these were encouraged. Similarly, the NSHealth/ICON project could provide an international vehicle for widespread use of passive samplers in European waters, and links with simultaneous biological effects measurements.

It was further suggested that the Organising Group should look to EU FP7 with a view to making a proposal for funding. Such a proposal should cover fresh as well as salt water. Finding an appropriate coordinator would be an essential early step.

8.2 Investigation of the particle affinity and bioavailability of PAHs in relation to coal tar pitch (CTP) using passive samplers

8.2.1 Introduction

This summary reports a study performed by the Norwegian Institute for Water Research (NIVA, by Kristoffer Næs and Anders Ruus) on the particle association and bioavailability of PAHs associated with coal tar pitch. Passive samplers are used to measure the dissolved free fraction of PAH in sediment pore water. Concentrations in sediment living invertebrates are predicted based on the measured free fraction and then compared to actually measured concentrations in the invertebrates. The study is directed related to the ICES passive sampling trial survey.

8.2.2 Background

Polycyclic aromatic hydrocarbons (PAHs) have been and are a prioritized group of environmental contaminants in Norway and abroad. In Norway, the point sources have primarily been discharges from aluminium- and ferromanganese-smelters using the Søderberg-anode. These discharges have been substantial and high concentrations of PAHs have been found in sediments and mussels in the vicinity of the smelters. Currently, focus is on PAHs, especially with regard to planning remedial measures for the contaminated sediments, in correspondence with implementation of the EU Water Framework Directive.

Although high concentrations of PAHs have been found in sediments in the vicinity of the smelters, the observed effects have been minor (Næs, 1998). It was hypothesized that the reason for this was that the PAH from smelters using the Søderberg-anode was adsorbed to particles to a much higher degree than what was reported. It is widely accepted that it is the dissolved fraction of pollutants that is available for interaction with biological tissues and thereby can cause bioaccumulation and/or biological effects. To further pursue this, the Norwegian Institute for Water Research took on a task to investigate the bioavailability of PAHs from sediments outside several Nordic smelters, using passive samplers for PAHs and investigating actual bioaccumulation in an experimental setup. The aims of the project were as follows:

1) Verify the partitioning constants for the passive samplers used in the measurements (POM-SPE).

2) Measurements of site specific partitioning coefficients for PAHs between sediment particles and water.

3) Quantification of the accumulation of PAH in bottom dwelling organisms. The rationale for this is to show if high partitioning coefficients correspond with reduced bioavailability (investigate correspondence to pt. 2, above).

Sediments used

Sediments were collected from the vicinity of four Norwegian and one Swedish aluminium smelter. Unpolluted sediment as a control/reference was collected from a clean site (in the outer Oslofjord) and underwent the same treatments as all other sediments. Finally, a spiked sediment (control-sediment, spiked with selected PAHs) were prepared, and tested correspondingly.

Organisms used

An established test system for the testing of bioavailability of contaminants in marine sediments (Hylland, 1996; Ruus *et al*., 2005; see reference for a detailed description) is used. The test system is used earlier in a number of occasions. The species studied in this experimental setup are the polychaet *Nereis diversicolor* and the gastropod *Hinia reticulata*. Polychaetes and molluscs represent two important groups in marine ecosystems. *N. diversicolor* is common along the coasts of Europe, from the Mediterranean to Helgeland (Mid Norway), and in the Baltic Sea. It is found primarily in shallow waters, where it can occur in dense populations. *Hinia reticulata* is also found in shallow waters and is common from the Canary Islands and the Azores in the south, to Lofoten (North Norway) in the north. Both species prefer sandy or muddy sediment and are tolerant to low salinities. *N. diversicolor* is omnivorous, while *H. reticulata* is a scavenger and a predator, but can also utilise organic matter in the sediment. *N. diversicolor* is one of the most studied marine invertebrates and has also been used in other bioaccumulation studies. For different reasons it was attempted to include a third organism. The protobranch bivalve *Nuculoma tenuis* was chosen, based on the following criteria:

1) It should be possible to obtain in sufficient numbers;

2) It should be a relevant bottom dwelling species, being a sub-surface selective deposit feeder.

8.2.3 Calculations

To elucidate the uncertainties associated with particle adsorption and bioavailability, analyses of dissolved fractions of PAHs in the sediments were performed with a SPE-method (POM-SPE) (Jonker and Koelmans, 2001; see reference for details). From the results, partitioning coefficients between the particular phase and the water phase (Kd) were calculated.

To account for the amount of organic carbon in the sediment and amount of lipid in the organisms, biota to sediment factors (BSAF)s were calculated:

$\mathrm{BSAF} = \frac{C_{lipid}}{C_{OC}}$, where C_{lipid} is the lipid normalized concentration in the organism, and C_{OC} is the organic carbon normalized concentration in the sediment.

Expected BSAFs were calculated from the POM-deduced K_d's according to:

$$\mathrm{BSAF} = \frac{C_{lipid}}{C_{OC}} = \frac{K_{lipid} \cdot C_W}{\left(\frac{C_S}{f_{OC}}\right)} \text{ where } C_W = C_S/K_d$$

where $C_W = C_S/K_d$

assuming the partitioning coefficient between organism lipids and water equals K_{ow} ($K_{lipid} = K_{ow}$).

8.2.4 Results

Sediment to water partitioning coefficients (K_{ds})

K_{ds} deduced using the POM-SPE method were higher than those derived from K_{ow}, using Free-energy relationship (following Karickhoff *et al*., 1979), anticipating 1% carbon in the sediment. More specific, K_{ds} deduced using the POM method were a factor 9 – 4079 (median = 49) higher, dependent on sediment and compound (median for Koc = 27). This difference-factor for the Kds was less pronounced in the spiked sediment, in which the PAHs seemed weaker adsorbed (a factor 5 – 36, dependent on compound).

Nereis diversicolor

Expected BSAFs calculated from K_{ds} deduced using POM, sediment concentrations (OC normalized) and K_{ow} (see pt. c. in Calculations, above) corresponded very good with the BASFs deduced from the actually measured concentrations in *N. diversicolor* (lipid normalized) and sediments (OC normalized). More specific, the expected BSAFs were a factor 0.11 – 13.8 (median = 1.1) higher than the actual measured BSAFs (varying with PAH compound and sediment).

Hinia reticulata
Expected BSAFs calculated from K_{ds} deduced using POM, sediment concentrations and Kow corresponded very good with the BASFs deduced from the actually measured concentrations in *H. reticulata* and sediments. More specific, the expected BSAFs were a factor 0.03 – 17.3 (median = 1.0) higher than the actual measured BSAFs.

Nuculoma tenuis
Expected BSAFs calculated from Kds deduced using POM, sediment concentrations and Kow corresponded not as good with the BASFs deduced from the actually measured concentrations in *N. tenuis* and sediments, as observed for the other two species. More specific, the expected BSAFs were a factor 0.014–0.35 (median = 0.05) higher (in other words a factor 2.9 – 71 (median = 20) lower) than the actual measured BSAFs.

It is good reasons to believe that the results for Nuculoma are artefacts due to contamination by particulate matter in the Nuculoma samples. These arguments is supported by the unusual high concentrations in that organism compared to Nereis and Hinia, the sediment similar PAH profile and physiology of the organisms. It is unlikely that the pattern observed in Nereis and Hinia should be a result of a higher capability than Nuculoma to metabolise and eliminate especially the higher molecular weight PAHs.

8.2.5 Conclusions

The results from the POM-experiments showed that the PAHs associated with the sediments in the vicinity of the smelters were stronger (a median factor of at least a magnitude) adsorbed/absorbed to the particles, than the Karickhoff *et al*. (1979) free energy relationship implies. This further implies that the bioavailable fraction is correspondingly lower, and one would expect lower bioaccumulated concentrations. The accumulated concentrations measured in *Nereis diversicolor* and *Hinia reticulata* did, in fact, show concentrations that were expected based on the POM-deduced sediment-water partitioning coefficients (Kds). Thus, the measured biota to sediment accumulation factors (BSAFs) agreed also very well with those expected from the POM-deduced K_{ds}.

On the other hand, this good correspondence was not observed for the third species, *Nuculoma tenuis*. There were however logistical intractability's connected to this species biology and

size, that render it probable that particulate sedimentary matter contaminated the *Nuculoma* tissues analyses. Exceptionally high PAH concentrations relative to the other two organisms and a PAH profile more similar to that of the sediments support this assumption.

Results from the project will be published in the open literature during 2007.

8.2.6 References

Hylland, K. 1996. Bioaccumulation of contaminants from marine sediments – Establishment of a test system. NIVA-report 3537. (In Norwegian).

Karickhoff, S. W., Brown, D.S., and Scott, T. A. 1979. Sorption of hydrophobic pollutants on natural sediments. Wat. Res., 241–248.

Næs, K. 1998. The distribution and effects on Norwegian fjord and coastal ecosystems of polycyclic aromatic hydrocarbons (PAHs) generated by the production of primary aluminium and manganese alloys. Thesis for the degree of Doctor Philosophiae.

Ruus, A., Schaanning, M., Øxnevad, S. and Hylland, K. 2005. Experimental results on bioaccumulation of metals and organic contaminants from marine sediments. *Aquat. Toxicol*., 72: 273–292.

8.3 Other possibilities for international cooperation.

In addition to the passive sampling trial survey, possibilities for further international cooperation on the use of passive samplers were discussed. At the moment several project are started or underway using this technique

8.3.1 Scotland

Kyari Yates, FRS continues to work on passive sampling in sediments. In addition to joining Kristoffer Naes and collecting samples in Vefsn fjord, he has also collected sediment samples on Loch Leven, Scotland. An aluminium smelter used to operate until a few years ago in Loch Leven, and for most of its period of operation discharged an effluent to the loch that contained PAHs. The smelter has now closed, and although the water of the loch is now relatively uncontaminated, the sediments contain high concentrations of PAH. Kyari has applied SR sheets in different ratios to sediments at 5 locations, and has also done bioaccumulation experiments with *Nereis.* He hopes to present results at the ICES ASC 2007.

During the summer of 2006, an MSc student, Megan Kennedy, at FRS applied the same approach to passive sampling of dredge spoils from several harbours around Scotland, The data have been written up as a thesis, but have not yet been prepared for further publication.

8.3.2 Sweden

In Sweden, a project is underway to investigate sources and fate of PCDD/Fs in the Baltic Sea. The background to the project is that, although substantial measures have been undertaken in industries and purification plants to reduce the input of PCDD/Fs to the Baltic, the dioxin/furan concentrations are not decreasing in Baltic fish with high fat contents. Due to EU regulations salmon and herring is not allowed to be exported from Sweden to other EU countries. In order to provide the information on the dissolved concentrations of PCDD/Fs, passive samplers (20–50 µm thick POM) have been put out on in coastal (transportation and accumulation) and offshore (accumulation) areas. Since the results of the project are due to be reported in the late autumn 2007 the findings may be presented at the next WGMS meeting.

8.3.3 INRAM project

In Belgium a four year project INRAM (Integrated Risk Assessment and Monitoring of micropollutants in the Belgian coastal zone) project financed by the Belgian Federal Science

Policy has started. The project aims to assess in an integrated approach the risks of micropollutants to Belgian coastal zone ecosystems and management. The passive sampling technique is used as an innovative technique to measure contaminants pressure in the environment. A large group of hydrophobic organics will be measured on nine sampling points with passive samplers. Passive sampling is also used as a tool for in lab toxicity tests at constant and environmentally relevant concentrations. Through the 'reverse' use of passive samplers toxicity assays will be performed with complex mixtures of contaminants. A presentation about the project was given by Els Monteyne in the WGMS meeting.

8.3.4 France

At the French Research Institute for the Exploitation of the Sea (IFREMER – Nantes), several studies are in progress on the use of passive samplers to improve understanding of the fate and bioavailability of hydrophobic organic contaminants to marine organisms at the sediment water interface.

Passive sampling experiments with low-density polyethylene (LDPE) strips were carried out to assess the diffusive mobility of PAHs and PCBs at the sediment-water interface in the Mediterranean Thau lagoon. LDPE strips were exposed under laboratory conditions to sediments collected in the lagoon and other strips were exposed, *in situ,* to the water at the sediment-water interface. By this approach, the diffusive exchanges at the sediment/water interface will be evaluated. The whole data set will be available within the next few months and the results should be available at the next WGMS meeting.

A new project began this year on the bioaccumulation of hydrophobic organic contaminants in the benthic fish, *Solea solea*. Fishes will be exposed under laboratory controlled conditions to natural surface sediments. The accumulation of contaminants in the organisms (levels, fingerprints) will be compared to their diffusive mobility, as determined by parallel exposure of LDPE strips to the same sediments. This experiment aims at assessing the role of the sediments as a direct source of contamination for benthic fish.

9 Review and report on current state of knowledge of the use of passive samplers in sediment to address the activity of biologically active substances in the sediment, including both hydrophobic organic contaminants and other substances (e.g. metals)

9.1 Passive sampling for hydrophilic substances

Ian Davies gave a brief overview of approaches that have been used to passive sampling for non-hydrophobic substances in sediment. The approaches were broadly categorized as DET, in which gels are exposed to sediments and allowed to equilibrate with the pore waters, and DGT in which the gels are supplemented by a binding phase (such as Chelex for metals).

He described that DET gels can be built into spear-like probes of various lengths and inserted into sediment cores or into the sea bed. After equilibration (e.g. overnight) the probe can be removed and the gel cut out of the frame. The gel can then be sectioned into rather smaller sections (e.g. 1.5–2 mm sections are very feasible) for analysis. The profiles are therefore much more detailed than can be obtained through conventional pore water sampling by squeezing or centrifugation of section of sediment cores.

He described an example of the detection of non-permanent narrow depth bands of elevated nitrate concentrations in pore waters of anoxic sediments. The bands would probably not be detected by conventional sampling, and were interpreted as arising from an imbalance between the processes of nitrification and de-nitrification in anoxic sediments that normally keep nitrate concentrations below detectable levels. The peak occurred at the junction between

sediments regions where iron reduction and sulphate reduction were the dominant modes of organic matter decomposition.

DGT gels contain a binding layer behind the diffusive gel layer. Different kinds of binding layers have been used, for example Chelex resin for metals, iron oxides for arsenic and phosphorus, and silver iodide for sulphide. The effect of having such a binding layer is that the gel probe then competes with other processes in the sediment for transient chemical species. An example was shown of the use of a sulphide probe in anoxic sea loch sediments. Sulphate concentrations remained constant in the upper 12 cm of the core, suggesting that sulphate reduction was not occurring. However, a silver iodide gel clearly showed the presence of sulphide in this part of the core, suggesting that sulphate reduction was occurring but that the resultant sulphide was being rapidly re-oxidised to sulphate. This was confirmed by measurements of the distribution of bacterial sulphate reduction down the core (by incubations with radio-labelled sulphate). The gel showed very high activity of sulphide in those deeper parts of the core where free sulphide was detected in conventional pore water samples.

There was also some general discussion of the usefulness of DGT samplers for metals in sea water. These were available from DRT Research, an offshoot of Lancaster University, and could be deployed in the sea to provide reliable estimates of the available metals (Cu, Pb, As, Zn, etc) in sea water.

DET and DGT technology development and application has been led from Lancaster University, UK. A list of recent publications involving that research group is given in 0

9.2 Activity of hydrophobic contaminants.

A paper of Reichenberg and Mayer was noted in which a concept was presented using activity as bio-availability parameter. They distinguished bioavailability in two different parameters, accessible quantity and chemical activity. The accessible quantity describes a mass of contaminants, which can become available. The chemical activity is the potential or "pressure" driving diffusion, sorption, and partitioning. Chemical activity is linked to fugacity and freely dissolved concentration can be measured with passive sampling. Basically this is the concept that was identified in previous WGMS and suggested as indicator.

Reichenberg, F., and Mayer, P. 2006. Two complementary sides of bioavailability: accessibility and chemical activity of organic contaminants in sediments and soils, Environ. Toxicol. Chem., 25: 1239.

10 Review and report on the progress of cooperative work between WGBEC to WGMS on (bio)availability and related issues to report on opportunities for cooperative work.

WGMS and WGBEC met during their 2006 meetings to discuss possible areas of collaboration involving passive sampling in water or sediment and biological effects measurements. Although it was recognized that there were areas of mutual interest, no clear way forward was found. On the margins of that meeting, FRS and CEFAS (UK) agreed informally to try to find a way to do some collaborative work within UK. An outline of a project has been developed, and they hope to find scope in current programmes to do this work in 2007.

Els Monteyne presented under agenda item 8.3, a proposal for a project INRAM to undertake an integrated risk assessment of micro pollutants in Belgian coastal waters. An important element of this project was the use of passive samplers. They would be used to measure dissolved micro pollutants in water at several locations. They would also be used as sources of stable concentrations of contaminants in experimental systems, to investigate the biological effects of the contaminants. The WG saw this as a valuable and interesting development,

combining the uses of passive samplers as both accumulators of contaminants in field sampling and as providers of controlled mixtures of contaminants in experimental systems.

Norway (Ketil Hylland) has been developing a proposal over the last few moths for a large international seagoing Workshop called NSHealth (or ICON). The objective is described (SIME 07/3/17) as:

"The objective of the ICON project is to assess the health of North Sea ecosystems with regards to anthropogenic contaminants and their biological effects by applying an integrated approach. This will be achieved through a stepwise process involving an international expert meeting with prospective project participants (10–11 May 2007), a compilation of relevant data existing in national and international databases (autumn 2007) and field studies carried out in representative North Sea areas and in reference areas outside the North Sea in 2008–2009. The field studies will include methods put forward through the guidelines for integrated monitoring and assessment of contaminants and their effects developed at OSPAR/ICES WKIMON I-III. New methods will be developed and applied in an integrated risk assessment frame work to indicate ecosystem health status with respect to hazardous substances. The results from a programme such as that indicated here, i.e. the use of integrated chemical and biological effect methods to develop ecosystem indicators, will be relevant to OSPAR CEMP activities and might be equally used under the forthcoming EU marine strategy."

The project comprises three phases:

a) an international expert meeting where research ideas for the workshop are presented by participating laboratories;
b) Data compilation for the locations and areas selected for study including all information available for offshore areas in the North Sea;
c) Field studies at the selected locations and areas.

As with previous large Workshops like BECPELAG, the organizers plan to provide a large and effective infra-structure within which observations can be made and research carried out. The proposal envisages several European countries making ship time available to visit and sample at locations from the Barents Sea to Spain during 2008–2009. Sampling techniques could include the use of caged fish and shellfish on the sea bed.

When the project had been presented at WKIMON, advice had been given that the project should include (inter alia) elements covering the integrated monitoring strategies of WGBEC and WKIMON (i.e. meet OSPAR's interests), and recent developments in approaches to monitoring including passive sampling, genomic methods, and measurements of lysosome fragility.

WGMS agreed that this project showed considerable potential as a vehicle for further development and wide scale application of passive sampling. The organizational and physical structure (ships, cages, etc) would greatly facilitate a broad scale survey, and could include several offshore areas (which were largely missing from PSTS). A particular benefit would be the opportunity to link passive sampling data with biological effects measurements carried out by other scientists. It was important to ensure that the ICON organizing group was fully aware of the requirements for passive sampling were adequately covered by the final experimental design. Nobody from WGMS was a member of the ICON group, although several members of WGMS had good contacts within the ICON group. Ian Davies and Foppe Smedes undertook to brief members of the ICON group from Scotland and the Netherlands before the meeting of the ICON group on 10–11 May, and to attend themselves if possible.

11 Review the draft Guidelines on the use of passive samplers, to be prepared intersessionally by members of WGMS and MCWG

WGMS welcomed the draft Guideline on the use of passive samplers in sediment that had been prepared intersessionally by Foppe Smedes and Ian Davies. WGMS felt that the document could be better targeted if it was more clearly concerned primarily with silicone rubber samplers. The WG therefore proposed minor amendments to the document to this effect. The revised document is included as Annex 8: .

The WG also agreed that it was premature to offer the text as a Technical Annex to OSPAR, as OSPAR had not yet adopted passive sampling in its monitoring and assessment programmes. Nevertheless, the WG was anxious that the document should become more freely available to encourage the use of passive samplers more generally in monitoring and research activities. It as therefore proposed that a dedicated website be created to hold this and other useful documents related to passive sampling. Ian Davies agreed to attempt to find funding for the creation of such a site, and Foppe Smedes agreed to operate the site.

12 Cooperative development of guidelines for CEMP

WGMS undertook a review of the draft Technical Annexes on the determinations of polybrominated diphenyl ethers, hexabromocycladodecane and alkylated PAHs. Sub-Groups formed from WGMS produced lists of comments, which were sent to MCWG to ensure that parallel developments occurred in the sediment and biota Technical Annexes.

12.1 Together with MCWG develop draft technical annexes on monitoring of polybrominated diphenyl ethers and hexabromocycladodecane in sediments following the structure of the existing technical annexes

A sub-group (Celine Tixier, Els Monteyne, Lucia Vinas and Ian Davies) was formed to consider the draft Technical Annexes on the determination of PBDEs and HBCD in sediment. A series of comments were prepared (see Annex 10:) and were sent to the MCWG to ensure that the changes to be proposed to the sediment Technical Annexes and the biota Technical Annexes were consistent.

The revised Technical Annexes on PBDEs and HBCD are attached as Annex 11: and Annex 12:

12.2 Together MCWG, review the existing technical annexes on PAHs and revise as appropriate to include alkylated PAHs

A sub-group of WGMS (Celine Tixier, Lucia Vinas, Els Monteyne and Ian Davies) was formed to undertake a review a revision of the draft Technical Annex on alkylated PAHs. A series of comments were prepared (see Annex 13) and were sent to the MCWG to ensure that the changes to be proposed to the sediment Technical Annexes and the biota Technical Annexes were consistent.

Completion of the revision of the technical Annex will be carried out intersessionally by the subgroup in collaboration with members of MCWG.

13 Develop proposals for background concentrations of alkylated PAHs in sediment

WGMS examined the data on alkylated PAHs held in the database of sediment analyses from areas considered as suitable reflections of background conditions. The data base had been originally created at WGMS 2004 and used to propose BCs for a range of metals and organic contaminants in sediment, and has been developed further since then.

WGMS found:

i) That there were relatively few data on alkylated PAHs in the database.

ii) That the data covered very limited geographical areas

iii) That some of the contaminant data were not accompanied by appropriate cofactors analyses.

iv) That there were several inconsistencies in the data (e.g. medians greater than maximum values, or less than minimum values) that gave rise to doubts about the reliability of the data.

WGMS concluded that it was not possible to use this information directly. Only Scotland, Norway and France felt that they had information available on alkylated PAHs in sediments from areas that could represent background conditions. The French data were from sediment cores in the Bay of Biscay, and was available in the database. New spreadsheets of data were obtained from home laboratories in Oslo and Aberdeen. The Norwegian data was from areas on the west coast, whereas the Scottish data where from the UK National Marine Monitoring Programme and were divided between locations on the east and west coasts. In some cases, data were expressed as totals of C1, C2, C3 etc compounds, and in other cases specific individual compounds were reported. This necessitated slightly different approaches to the three data sets. The data were treated as follows:

Norway:

1) When instead of NAPC1 individual alkylated naphthalenes were reported, these data for individual mono-methylated compounds (2) were summed to derive an expression for NAPC1. If the values were <DL, the DL was taken into the sum.

2) Similarly for dimethyl naphthalenes, 3 individual compounds were summed to give NAPC2 for cases where no NAPC2 was reported

3) For trimethyl naphthalenes, 4 individual compounds were summed to give NAPC3.

4) There were no cases where a complete set of individual alkylated phenanthrenes were available so only the reported PACx values were included

5) All results were normalised to 2.5% CORG.

6) The concentrations in areas identified by NIVA as from background areas were, surprisingly, rather high in comparison to data from many other areas. Consequently, the 10% percentile of all data was calculated.

Scotland:

1) The data set consisted of 3–5 replicate samples from each of 4 stations, once per year for five years. Data below detection limit were listed as 0. These were included in the calculations, but in the few cases when data for a certain parameter from a station only showed values below detection limit, the lowest measured value of the whole dataset was used.

2) All data were normalized to 2.5% CORG. The median value was calculated for each station for each parameter, and then the median of the stations was calculated.

France:

> French data were not normalised and were used as they were recorded in the database. As the samples were muds, this is unlikely to introduce large errors. For data below detection limit, the DL was used, and median values were calculated for each parameter.

An initial set of proposed Background Concentrations were estimated as the median of the 10% percentile of the Norwegian data, and the medians of the Scottish and French data. The concentrations are tabulated below:

Table 13.1. Proposed Background Concentrations for alkylated PAHs in sediments, expressed as concentrations normalized to 2.5% organic carbon.

PARAMETER	CONCENTRATION (UG/KG DRY WEIGHT)
NAPC1	1.7
NAPC2	2.3
NAPC3	5.0
PAC1	4.5
PAC2	8.3
PAC3	9.9
DBT	1.3
DBTC1	2.3
DBTC2	5.0
DBTC3	4.8

WGMS recognized that these Background Concentrations had been obtained from very limited datasets and so they could not have high confidence in the values. WGMS recommended that they be forwarded to OSPAR with a view to them being used on a trial basis in data assessments.

WGMS also recommended that work be undertaken to extend the data set underlying these estimations, to include data from other areas, such as the Baltic Sea and to add the data to the database created in 2004. New data had been identified by Norway, UK and Sweden. The WG agreed to address the problem intersessionally. The work would be led by Carla Palma and Els Monteyne. The first steps in the process would be:

1) To obtain extracts of data on alkylated PAHs and cofactors from the 2004 database and seek confirmation of their accuracy from the originating laboratories
2) To identify sources of data from areas considered to represent background conditions
3) To collate data on contaminants and appropriate cofactors from these areas
4) To submit these data to the 2004 database, to add to or replace the existing data, as appropriate.

14 Provide expert knowledge and guidance to ICES Data Centre on a continuous basis

In response to a request from the ICES Data Centre, WGMS would like to state that the current use of METEX from ERF2.2 is for the interpretation of metal data from sediment to distinguish between total digestion and levels of partial digestion (with hydrofluoric acid or other strong acids). This was all extractable from the METX 2.2 and OSPARMON prepared a dictionary in the normalisatio data base to convert METEX code into digestion level.. This table will have to be redone using information from METCX (extraction) and METOA (analyses method). For example NAA in METEX 2.2 is an analytical method en no extraction/digestion and will move to METOA, and from METCX there is no info if a total concentration is obtained. This translation from METEX to METCX and METOA might be scientifically justified but will require another workaround for the OSPAR-MON assessments. In addition MON will also have to use information from the METOA code. In the way extraction and analytical method are separated presently that is not to complicated as all methods that do not digest are so-called "Total methods". It may be suggested that when METEX 2.2 was NAA or XRF the METCX field may be filled with "Total".

To ensure that the transfer of ERF2.2 format data into 3.2 format data is possible without loosing information, the codes could be checked before transferring of data to DOME, and any not in use in the 2.2 format should be removed from the list. In Annex 14: a list of METEX 2.2 codes for metal analyses is given, indicating the level of digestion and the number a HM parameter is reported using that method.

A revised translation table is given in Annex 14: (METEX conversion table1.xls). This gives the translation between METEX and METCX (+METOA where necessary). Only NEC in format 2.2 is not uniquely identified by METCX+METOA by this approach, after inclusion of the amendments to METCX table. It may be considered if the slurry/suspension methods (SST, SAN and SAT) are also analytical methods more than extraction?

15 Any other business

15.1 Contributions for ASC Theme session on Passive Sampling

Contributions were offered for the ASC Theme Session J on passive sampling as follows:

1) Design of the ICES passive sampling trial survey (PSTS) 2006–2007.
2) ICES intercalibration of passive sampling in water and sediment.
3) Preliminary interpretation of field data from the ICES passive trial survey (PSTS).
4) Use of DGT in monitoring programmes for metals in seawater.
5) Availability of PAHs in sediments from the Vefsn Fjord, Norway to the lug worm, *Nereis virens*.
6) Measurement of the availability of PAH compounds in marine sediments and pore-waters from Loch Leven, Scotland using silicone rubber passive samplers.
7) Variation of sampling rate with partition coefficient.
8) Yossi Kukonen – biological activity of hydrophobic contaminants.
9) Effect of biofouling on sampling rates of passive samplers.
10) Dioxin transport in fjords.
11) Partition coefficients of PAHs in sediments contaminated by coal tar pitch from aluminium smelters.

Members of the WG were encouraged to offer further contributions to the Theme Session to ensure that it is a success as an initial venue for presentation of further results from PSTS, and for the publicising of other aspects of work on passive samplers.

15.2 International QA for passive samplers

Foppe Smedes informed the WG that Wim Cofino and Steven Crum of QUASIMEME had visited him and discussed the possibility of including passive samplers in the analytical matrices in QUASIMEME exercises. No document describing the possible structure of an LPS study was available, although Foppe Smedes reported that QUASIMEME had appeared enthusiastic. The WG agreed that coordinated LPS were missing for passive samplers and that a QA system would be necessary before passive sampling could be formally adopted, for example by OSPAR. However, they noted that the fee should be at a level that would not deter potential participants. WGMS recommended that QUASIMEME be encouraged to develop a design for an LPS for passive sampling.

15.3 Publications on the *Prestige* incident

Lucia Vinas made three papers available to the WG concerning monitoring activity in water, sediment and mussels around Spain after the Prestige accident.

16 Recommendations and Action list

Actions and recommendations and were collected during the meeting and collated in Annex 15: and Annex 16: respectively.

17 Election of a chairman

Foppe Smedes has served as Chair for six years, and has been leading the WG through a time of significant growth and success. He took on the task as the long-running problems of normalisation began to show real signs of progress towards solution after the meetings chaired by his predecessor, Steve Rowlatt. Normalisation and related matters are now established in OSPAR assessment procedures. Recent years have shown increasing interest in passive sampling in sediment, and also in water and have resulted in a large scale international field trial run jointly by members of WGMS and MCWG. The initial results of this exercise are described in this report.

In view of the need to retain as much confidence as possible that the PSTS results will be taken to their conclusion, both at ASC2007 and afterwards, the WG recommends that the 2008 meeting be chaired by Foppe Smedes, with the assistance of Patrick Roose as Co-Chair, with the intention that Patrick Roose be invited to take on the chairmanship after the 2008 meeting.

18 Date and venue of the next meeting

WGMS recommend that they should next meet at IOE, Vigo, around March 2008 and thanked Lucia Vinas for the invitation she had offered to the WG on behalf of her Director.

19 Closure of the meeting

The meeting closed at 12:25 on Friday 23 March 2007, after thanks had been expressed to Stefan Schmolke for acting as host and to Foppe Smedes for his continuing enthusiastic leadership. Furthermore the very active role of Ian Davies in preparation and editing of the summary record is highly appreciated.

Annex 1: Agenda of WGMS

27th meeting of the ICES Working Group on Marine Sediments in relation to pollution

Hamburg (Germany) 19 -23 March 2007 Acting chair Foppe Smedes

Start at 1000, 19th of March and 900 for the other meeting days.

Closure of the meeting is foreseen at 13:00, 23 March

1	Tor	Opening of the meeting WGMS meetings may be opened with some reflection on the 2006 meting. Feedback on our work by other groups.
2		Adoption of the agenda After agreement on the items on the agenda and their contents, a working schedule and appointment of rapporteurs will be arranged Review Actions list and Recommendations
3	a	review and comment on the report of the data assessment from the 2006 meeting of OSPAR/MON in relation to sediments
4	c	Evaluate available information on the role of sediment chemistry in AMAP assessment and monitoring activities
5	k	to review recent developments in the assessment of sediment quality in the Barents Sea.
6	h	review the progress of the OSPAR One-off surveys, or, if already available, evaluate the data in collaboration with WGSAEM and MCWG
7	g	continue the collection of information on different estuaries and case studies of the interpretation of monitoring data, taking into account sediment dynamics.
8	f	Evaluate intersessional activities on passive sampling methodologies; i.e. (i) evaluate, with MCWG progress and outcome of passive sampling trial survey (PSTS) for water and sediment including intercalibration, (ii) small field trial on contamination by smelter discharges, and (iii) other possibilities for international cooperation.
9	i	to review and report on current state of knowledge of the use of passive samplers in sediment to address the activity of biologically active substances in the sediment, including both hydrophobic organic contaminants and other substances (e.g. metals)
10	d	Review and report on the progress of cooperative work between WGBEC to WGMS on (bio)availability and related issues to report on opportunities for cooperative work.
11	e	Review the draft Guidelines on the use of passive samplers, to be prepared intersessionally by members of WGMS and MCWG
12	l	Cooperative development of guidelines for CEMP, (i) together with MCWG develop draft technical annexes on monitoring of polybrominated diphenyl ethers and hexabromocycladodecane in sediments following the structure of the existing technical annexes. (ii) together with WGBEC and MCWG, review the existing technical annexes on PAHs and revise as appropriate to include alkylated PAHs
13		develop background concentrations for the following alkylated PAHs in sediments and biota:
	13.1	C1-, C2- and C3-naphthalenes;
	13.2	C1-, C2- and C3-phenanthrenes, and;
	13.3	C1-, C2- and C3-dibenzothiophenes, as well as the parent compound dibenzothiophene;
14	j	provide expert knowledge and guidance to ICES Data Centre (possibly via sub-group) on a continuous basis

15 Any other business

15.1 Theme session on passive sampling at ASC 2007

15.2 Expression of interest of QUASIMEME for LPS on passive sampling

15.3 Papers available on the “Prestige” incident.

16 Recommendations and Action list

17 Election of a new chair

18 Date and venue of the next meeting

19 Closure of the meeting
Intended closure time is Friday 23 March at 1300

Annex 2: Terms of reference for WGMS 2007

2006/2/MHC05 The **Working Group on Marine Sediments in Relation to Pollution** [WGMS] (Chair: F. Smedes, Netherlands) will meet from 19–23 March 2007 in Hamburg, Germany, to:

d) review and comment on the report of the data assessment from the 2006 meeting of OSPAR/MON in relation to sediments;

e) develop background concentrations for the following alkylated PAHs in sediments and biota:

(i) C1-, C2- and C3-naphthalenes;

(ii) C1-, C2- and C3-phenanthrenes, and;

(iii) C1-, C2- and C3-dibenzothiophenes, as well as the parent compound dibenzothiophene;

f) receive information on the role of sediment chemistry in AMAP assessment and monitoring activities

g) review and report on the progress of cooperative work between WGBEC to WGMS on (bio)availability and related issues to report on opportunities for cooperative work;

h) review the draft Guidelines on the use of passive samplers, to be prepared intersessionally by members of WGMS and MCWG;

i) evaluate and report on the progress of work planned by various participants in field trials discussed at WGMS 2006 in relation to (bio)availability of organic contaminants in sediments using passive sampling methodologies; i.e. (i) evaluate, with MCWG collaborative work of MCWG and WGMS members to perform a passive sampling trial survey (PSTS) for water and sediment including intercalibration, (ii) small field trial on contamination by smelter discharges, and (iii) other possibilities for international cooperation.

j) continue the collection of information on different estuaries and case studies of the interpretation of monitoring data, taking into account sediment dynamics;

k) review the progress of the OSPAR One-off surveys, or, if already available, evaluate the data in collaboration with WGSAEM and MCWG;

l) to review and report on current state of knowledge of the use of passive samplers in sediment to address the activity of biologically active substances in the sediment, including both hydrophobic organic contaminants and other substances (e.g. metals)

m) provide expert knowledge and guidance to ICES Data Centre (possibly via sub-group) as requested;

n) to review recent developments in the assessment of sediment quality in the Barents Sea.

o) together with MCWG, to carry out the following development work with regard 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) to ensure that monitoring guidance is in place to support a revised Co-ordinated Environmental Monitoring Programme.

i) develop draft technical annexes on monitoring of polybrominated diphenyl ethers and hexabromocycladodecane in sediments following the structure of the existing technical annexes. SIME 2007 will be invited to clarify the congeners and compartments that are relevant for the development of monitoring guidance for brominated flame retardants.

ii) together with WGBEC and MCWG, review the existing technical annexes on PAHs to see whether they are adequate for monitoring of target alkylated PAHs and, as appropriate, prepare advice on any revisions that are necessary.

WGMS will report by 2 April 2007 for the attention of the Marine Habitat Committee and ACME.

Supporting Information

PRIORITY:	This Group handles key issues regarding monitoring and assessment of contaminants in sediments.
SCIENTIFIC JUSTIFICATION AND RELATION TO ACTION PLAN:	Action Plan Nos 1.7, 1.10, 1.11, 2.8, and 4.12 a) The OSPAR/MON assessment of 2005 started to give attention to the interpretation of the assessments in relation to spatial differences and causes. Developments through WGSAEM may increase the ability of assessors to integrate data across regions. Anticipating that the report of the proposed 2006 assessment will be available before the meeting, WGMS can review the progress made. b) This is in response to an OSPAR request. c) As part of its responsibility for advice on sediment quality assessment, WGMS considered that there would be benefit in taking a wider view of related activities in sea areas outside those normallt covered by OSPAR assessments, with a view to identifying areas of commonality and procedures/concepts that could usefully be transferred bewteem AMAP and CEMP. d) WGMS and WGBEC in 2006 developed initial steps towards collaboratiove work in the application of passive sampling to biological effects studies. This agenda itam will review the intersessional progress of the interaction,and consider the need to make further plans for cooperation on integrating chemical and biological effect measurements at a research level and subsequently at monitoring/assessments levels; e) The proposed joint field trials of passive samplers in association with MCWG (and potentially WGBEC) depend on the development of practical Guidelines for the preparation, use and analysis of passive samplers. The Guidelines will be drafted intersessionally, but will require formal review by the full WG. f) The planned work can be discussed under three headings, as indicated in the ToR. The WGMS will review the work and contribute practically in both the analytical and interpretive work. Futhermore to evaluate possible use in monitoring in future. g) The finalised annex to the Sediment Monitoring Guidelines will assist ICES in providing advice to others, e.g., OSPAR and HELCOM, on the incorporation of sediment dynamics in the interpretation of sediment monitoring data. However a revision in future is foreseen and therefore WGMS will continue to collect information and examples on the subject; h) WGMS 2005 provided detailed advice on the performance of the OSPAR One-off surveys for “new” contaminants and is very eager to follow the process, learn more from it with a view on improving the design for possible future surveys. If data are available, WGMS, in cooperation with MCWG and WGSAEM is an appropriate forum for evaluation of the data; i) Methodologies for sediment assessments in terms of (bio)availability are developing rapidly. WGMS should continue to receive reports of developments in the area of hydrophobic organic chemicals, and also start to consider other substances, such as metals. This would be undertaken with a view to extending the draft Guidelines being reviewed in item d) above to include hydrophilic substances. j) This is in compliance with a continuing requirement from the ICES Data Centre in relation to the development of DOME and associated software. k) Data on sediment contamination in the Barents Sea presented by the Russian delegate at WGMS 2006 showed interesting parallels, and differences from surveys of similar nature in less northerly areas. The WG wish to review the furtehr development of this work with a view to informing assessment procedures used by OSPAR MON. l) This is a response to an OSPAR request (OSPAR 2007/2)

RESOURCE REQUIREMENTS:	None required.
PARTICIPANTS:	-
SECRETARIAT FACILITIES:	None required
FINANCIAL:	None
LINKAGES TO ADVISORY COMMITTEES:	ACME
LINKAGES TO OTHER COMMITTEES OR GROUPS:	WGBEC, MCWG
LINKAGES TO OTHER ORGANISATIONS:	OSPAR, HELCOM

Annex 3: List of participants

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Annex 4: Review of Recommendations from WGMS 2006.

2006 Ag. It.	WGMS2006 recommendation	Progress recorded by WGMS2007.
3	WGMS supports the process of yearly assessments by OSPAR-MON to become a routine operation. For the 2005 report, more explanation on graphs, as indicated in WGMS report, would be helpful.	Annual assessments by OSPAR MON are planned for 2007 and 2008. Annotations of graphs have been improved.
3	WGMS recommended that the proposed review of EACs be undertaken as a matter of some urgency, as they considered it important that the draft EACs are confirmed or amended, and that guidance is developed on the interpretation of the relationships between field data and EACs.	This is in hand through SIME
3	WGMS recommends that the data available at PINRO are submitted to the ICES database to be used in future assessments	No information available
4	WGMS recommends that WGBEC and WGMS work in cooperation to develop intersessional activities on the use of passive sampling in connection with biological effect measurements. When desirable and possible, inclusion of effects measurements could be considered in the trial-survey suggested under Agenda Item 6 (Action 5).	Some plans have been made between FRS and CEFAS but not yet put into operation. The NSHealth/ICON should provide another opportunity to combine BE and PS.
5	WGMS concluded that they should continue to work on the application of passive sampling, using reference phases, as a tool for measuring the availability of contaminants in sediment and as a monitoring and research tool. (Attention to comparison and/or standardisation and or QA) (Action 2).	WGMS members have continued this work through PSTS and other projects.
6	WGMS recommends that a subgroup consisting of members of MCWG and of WGMS will work intersessionally to guidelines for passive sampling of hydrophobic contaminants in water and sediment (Action 6).	WGMS members prepared a document on sediment sampling.
	WGMS recommends that a trial survey on the use of passive sampling for hydrophobic contaminants be organised, as designed by MCWG and WGMS. This should include water, sediment and a laboratory intercalibration (Action 6).	The PSTS took place and data collation and interpretation continues.
8	Following the recommendation made in 2005, WGMS recommends that the completed document "Sediment Dynamics in relation to sediment trend monitoring" (Annex 6 to the ICES WGMS Report 2005) on the interpretation of sediment trend monitoring data with regard to sediment dynamics should be forwarded to MHC/ACME for inclusion as an annex to the ICES Sediment Monitoring Guidelines (Action 9).	Some misunderstanding occurred between WGMS and MHC and the document will be presented to ACME in 2007.
9	WGMS recommends to review data emerging from the One-off surveys of Endosulfan, 2,4.6-TriTertiary butylphenol and SCCP.	This is an item on the agenda for WGMS 2007.
10	WGMS recommends that the sediment data available for REGNS to be updated with new submissions (Action 11). REGNS to explain how the sediment data have been processed and used in order for WGMS to contribute more effective to the REGNS process.	REGNS indicated that they were content with the data that they had and required no update. WGMS2007 approached ICES for information but no response form REGNS was recorded. REGNS has dissolved in 2006.

Annex 5: Review of Action List from 2006 report

Item	Action point	Action taken
1	Andrey Zhilin to investigate the possibilities to report data from Barents Sea to ICES	A further report on the Barents Sea sediments has been supplied for WGMS 2007.
2	Members to report at the next meeting on activities towards the use of passive sampling techniques of hydrophobic contaminants including validation studies	Various activities will be reported at WGMS 2007
3	Ian Davies to report on methods that address the activity of metals in (pore)-water	An introduction to the subject will be provided during the 2007 meeting
4	All members to collect examples where the (bio)availability of metals is studied in a promising way.	Some members have contribution to make at the 2007 meeting
5	Foppe Smedes to coordinate intersessional activities, involving passive sampling, evolving from cooperation with the WGBEC.	This activity has been successful and information is available for the 2007 meeting
6	The joint MCWG and WGMS subgroup to write draft guidelines for passive sampling and, following the suggestion of SIME 2006, to organise a field trial	WGMS took the lead on sediment guidelines, and a draft is available for the 2007 meeting. MCWG lead on water.
7	Members to consider participation in the trial survey on passive sampling of hydrophobic contaminants in water and sediment.	Several members have participated in the trial survey.
8	Birgit Schubert to supply the group with information about activities in Germany concerning sediment dynamics in relation to monitoring	Birgit provided a poster for the meeting, but was unable to attend herself.
9	The Chair to bring the Annex 6 of WGMS 2005 report under the attention of the Chair of the MHC.	There had been some misunderstanding between the Chairmen of WGMS and MHC and this item has been carried forward to ACME 2007.
10	All relevant members to continue with the collection of information and examples on the subject of sediment dynamics.	Some members have brought information to the 2007 meeting.
11	Foppe Smedes to update the sediment data for REGNS before 1 May 2006 in the same way as described in Agenda Item 9 of WGMS 2005 report. Also the errors given will be updated following the new developed calculation.	REGNS system decided that they did not need to update their databases at this time.

Annex 6: Polycyclic aromatic hydrocarbons (PAHs) and organochlorines (OCs) in bottom sediments of the Barents Sea

Polycyclic aromatic hydrocarbons (PAHs) and organochlorines (OCs) in bottom sediments of the Barents Sea

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The Barents Sea supports rich and unique ecosystems, and marine resources of several species of fish, shellfish and crab are exploited. The west areas of the Barents Sea are important habitats and feeding grounds for commercially important fish species. In addition to local sources, the region is subjected to long-range transported pollutants from industrialised areas further south in Europe, both through the atmosphere and through the ocean currents. Anthropogenic contamination of remote regions of the world, such as the Arctic, by PAHs and persistent organochlorine compounds (OCs) has been recognised for several decades. Temperature-dependent physicochemical properties of semivolatile organic compounds are believed to make them more prone to long-range atmospheric transport and accumulation in Arctic waters.

Contaminant concentrations in bottom marine sediments represent a critical measure of health for any coastal ecosystem. The sediments are a significant reservoir for hydrophobic contaminants and reflect the input of them to the ecosystem. The purpose of the present investigations was to determine PAH and OC contamination levels and distribution patterns in the bottom sediments from the north-western area of the Barents Sea and to compare with those from the adjacent areas. An attempt to evaluate the toxicity of concentrations measured has also been made.

Surface sediment samples were collected in the Spitsbergen area and adjacent areas during the expedition of the Knipovich Polar Research Institute of Marine Fischeries and Oceanography (PINRO) onboard R/V "Fridtjof Nansen" in August–October 2005. The sampling covered 38 stations (Figure1).

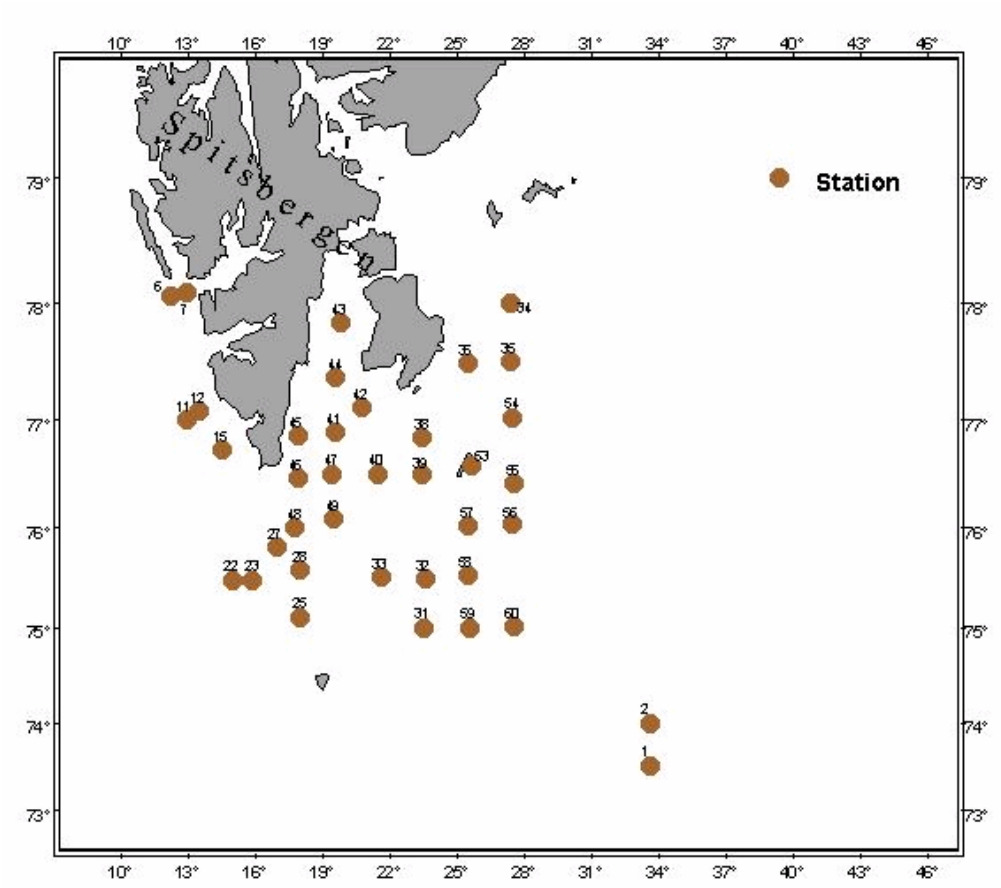

Figure 1. Sediment grab stations in the Barents Sea (R/V "F. Nansen" cruise, August–October 2005).

Sediments were retrieved by a 0.1 m^2 van Veen grab. Sub-samples of the 0–1 cm layer were collected from the grab samples with a stainless steel spoon for PAH, OCs and grain size analysis. All samples were stored in specially cleaned glass jars and frozen at −20 °C.

Grain size distribution was determined for 26 samples gravimetrically after wet sieving. (Table 1). Sediment water content was determined after drying a sample to constant weight (for 4 days at 50 °C).

Table 1. Grain size composition of bottom sediments, August–October 2005

Station	Depth (m)	Grain size composition (%)		
		Gravel >1 mm	Sand 1–0.063 mm	Silt+clay <0.063 mm
1	280	0,7	39,0	60,4
2	333	0,7	41,0	58,2
7	219	9,9	13,0	77,1
12	416	0,7	8,6	90,7
22	380	7,2	37,0	55,8
23	302	12,1	32,7	55,2
25	142	1,3	43,0	55,7
28	138	21,9	35,8	42,3
32	86	37,6	31,3	31,1
34	196	1,7	13,0	85,2

36	104	15,0	11,8	73,2
38	108	0,8	43,0	56,2
39	102	0,9	42,3	56,8
40	230	0,5	23,0	76,6
41	151	1,7	24,7	75,6
42	73	0,6	17,8	81,6
43	51	23,1	58,7	18,2
44	144	2,7	16,7	80,6
45	142	39,2	8,3	52,5
47	240	0,9	16,2	82,9
48	285	0,5	31,9	67,5
49	171	0,5	29,5	70,0
53	35	0,6	98,0	1,4
56	236	0,5	37,9	61,6
57	130	10,5	73,6	15,9
59	200	5,2	54,0	40,8

The procedure used for the analysis of PAHs is based on the International Oceanographic Commission guidelines with minor modifications. Individual sediment samples (20 g) were homogenised, treated with ethanol and KOH, and refluxed for 1.5 h together with a 1.0 ml solution of four deuterated PAHs. This solution included the following PAHs, obtained from the Sigma-Aldrich, Inc.: naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, perylene-d_{12}. The solid fraction was removed by filtration and the elute containing PAHs was extracted with hexane. The extracts were purified by column chromatography and eluted with hexane. The final extract was analysed by capillary column gas chromatography with mass spectrometric detection (Agilent 5973/6890N Gas Chromatograph equipped with a split/splitless injector and a 30m×0,25mm ID HP-5MS column, and G 1701A software for MS ChemStation). Detection limits were determined based on procedural blanks (blind samples) and for each of the aromatic compound varied from 0.005–0.20 ng/g dry wt.

The method involved air drying of samples, extraction with acetone–hexane mixture (40:50 by volume) by high-energy ultrasonic disintegration, and repetition of the extraction. The sediment extracts were purified with sulfuric acid treatment and copper filings to remove organic interfering compounds. The individual PCB congeners and pesticides were determined by gas chromatography (HP 5890) against the corresponding individual standards obtained from: Promochem, Sweden (PCBs, chemical purity 99%) and Supelco (pesticides, chemical purity 99%, Bellefonte, PA, USA).

A HP chromatography work station connected to the gas chromatograph was used for identifying chlorinated compounds. The analytes were: 12 polychlorinated biphenyl (PCB) congeners, 28, 31, 52, 99, 101, 105, 118, 138, 153, 156, 180 and 187; hexachlorobenzene (HCB); the DDT group (*p,p′*-DDE, *o,p′*-DDD, *p,p′*-DDD, *o,p′*-DDT and *p,p′*-DDT); and the HCH group (α- and γ-).The detection limit was 0.05 ng/g for each compound determined.

Both PAH and OC analyses were performed at PINRO analytical laboratory, Murmansk, Russia. Since 1999, the laboratory has participated successfully in the Quality Assurance Laboratory.

Table 2. Polycyclic aromatic hydrocarbons (ng/g dry wt.) and organochlorines (ng/g dry wt.) in bottom sediments from the Barents Sea; data show range and arithmetic mean.

Compounds	Abbreviations	*n*	Range	Mean
Naphthalene	Naph	28	1.4–188	48.3
Acenaphthylene	Acl	38	0.3–2.7	1.1
Acenaphthene	Ac	38	1.2-27.9	9.6
Fluorene	Fln	38	5.1-163	45.1
Phenanthrene	Phe	38	12.0-319	113
Anthracene	An	38	1.0-8.5	3.7
Fluoranthene	Flt	38	3.2-98.1	45.6
Pyrene	Py	38	5.0-82.4	39.7
Benz(a)anthracene	BaA	38	1.6-43.5	13.8
Chrysene	Chry	38	15.0-257	101
Benzo(b)fluoranthene	BbF	38	11.6-153	48.1
Benzo(k)fluoranthene	BkF	38	1.6-26.9	11.9
Benzo(a)pyrene	BaP	38	2.1-19.2	9.1
Indeno(1,2,3-cd)pyrene	Ipy	38	4.9-73.0	25.3
Dibenzo(a,h)anthracene	DBA	38	2.5-31.2	12.0
Benzo(g,h,i)perylene	Bper	38	6.7-71.9	35.6
Total PAH	∑PAH	38	117-1261	563
Total carcinogenic PAH[a]	CPAH	38	29.3-339	120
Phe/An		38	7.7-16.2	10.6
Flt/Py		38	0.8-2.0	1.2
HCB		38	0.17-1.55	0.78
α-HCH		38	0.17-1.44	0.44
γ-HCH		38	0.07-1.98	0.41
∑HCH[b]		38	0.27-2.26	0.85
p,p'-DDE		38	0.14-1.22	0.50
o,p'-DDD		38	0.05-0.30	0.09
p,p'-DDD		38	0.05-0.30	0.10
o,p'-DDT		38	0.05-0.29	0.11
p,p'-DDT		38	0.05-0.49	0.15
∑DDT[c]		38	0.36-1.79	0.95
∑PCB[d]		38	0.7-5.12	1.61

aCPAH - sum of benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, indenow(1,2,3-cd)pyrene and dibenzo(a,h)anthracene.

b ∑HCH - sum of α- and γ-HCH.

c ∑DDT – sum p,p'-DDE, o,p'-DDD p,p'-DDD o,p'-DDT and p,p'-DDT

d ∑PCB - sum of congeners 28, 31, 52, 99, 101, 105, 118, 138, 153, 156, 180 and 187.

The results obtained in north-west part of the Barents Sea and in Spitsbergen area were compared with literature and our data on PAH levels in bottom sediments from the different parts of the Barents Sea. The sum of parent PAHs of molecular mass 128–278 as well as levels of CPAH and Total TEQ have been used for comparison. The average levels of ∑PAH, CPAH, and Total TEQ found in bottom sediments from north-west part Barents Sea were higher than in sediments from others unpolluted sediments of fjords and bays and open parts of the Barents Sea.

Similarities and differences between the composition of the PAH components can be used as chemical fingerprints to identify potential sources. Phenanthrene and chrysene were predominant in sediments from all stations from the Barents Sea (Figure 4).

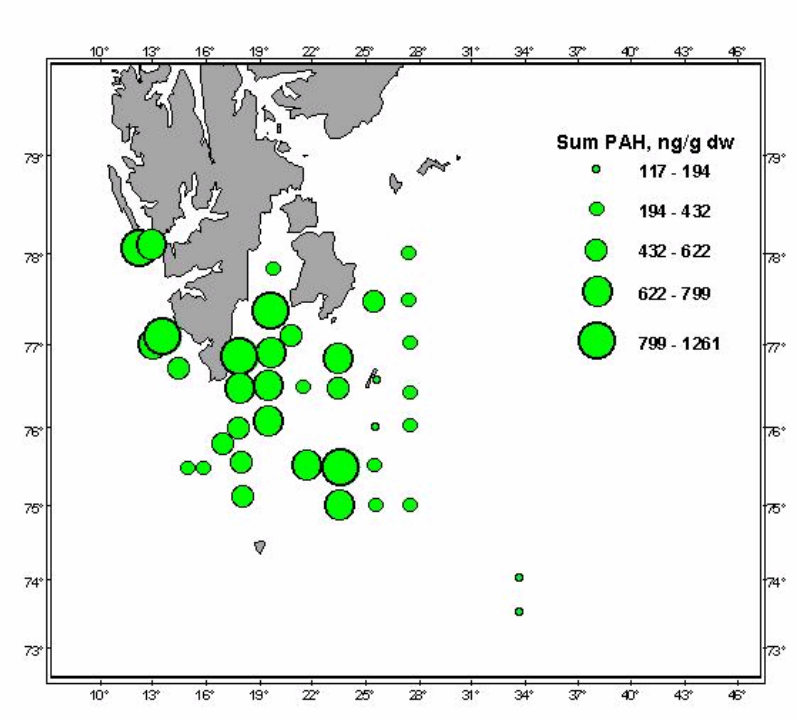

Figure 2. Content of PAH's in bottom sediments from the Barents Sea (August-October 2005).

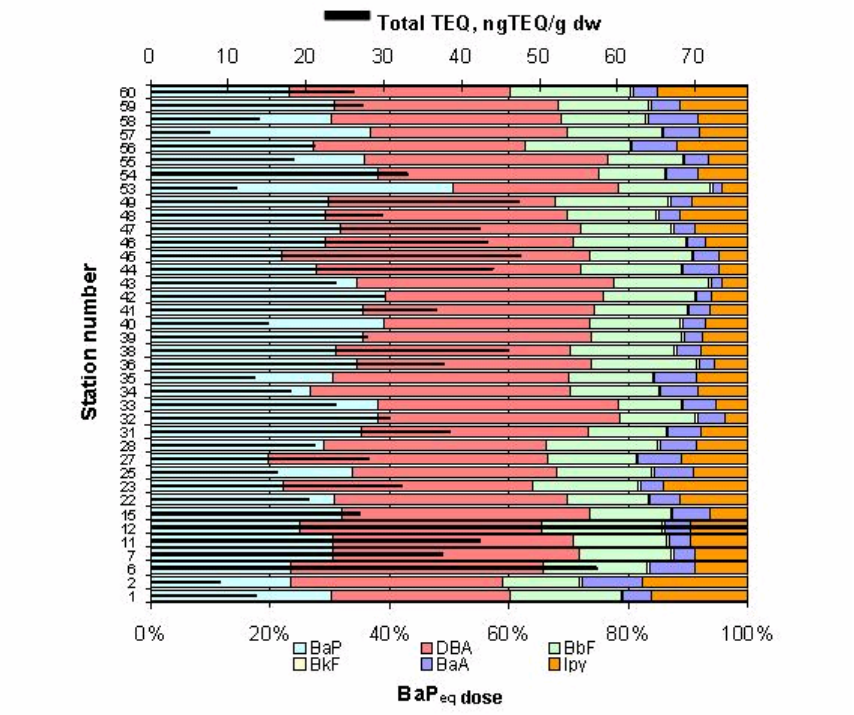

Figure 3. Total benz(a)pyrene-equivalent toxicities and relative contents of toxic benzo(a)pyrene doses of potentially carcinogenic PAHs in bottom sediments from Barents Sea.

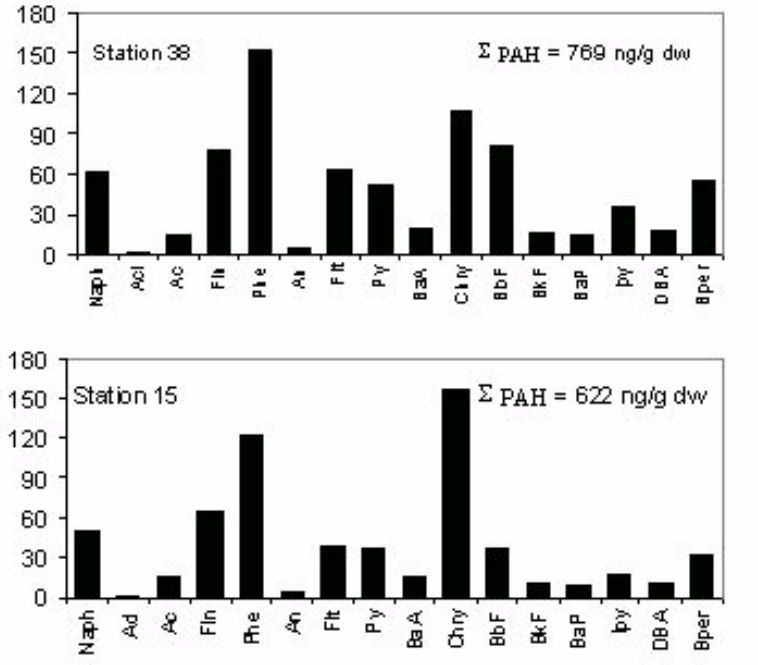

Figure 4. Characteristic PAH fingerprints of sediments from the Barents Sea.

Each of these compounds accounted approximately for 6-26% of ∑PAH. The exception was the samples from stations 1 and 2, where naphthalene dominated. In addition, benzofluoranthenes were among dominant compounds in sediments from station 53 and 60. Fluoranthene is a universal product of combustion of organic matter and is present in fossil fuel products. Phenanthrene has petroleum, combustion, and diagenetic origin. Phenanthrene/anthracene and fluoranthene/pyrene ratios have been used in order to distinguish between PAHs of diverse origin. The phenanthrene/anthracene ratio is temperature dependent. Predominance of fluoranthene concentration over pyrene is classically related pyrolytic origin, namely coal combustion. The phenanthrene/anthracene ratios calculated for all samples from Barents Sea were higher 7, and fluoranthene/pyrene ratios in most cases were not lower than 1.0 (Table 2), which indicate the pyrolytic origin of the predominant PAH compounds.

PAH compounds with low molecular mass (phenanthrene, anthracene, and acenaphthene) and PAH compounds with high molecular mass (benzofluoranthenes, benzo(g,h,i)perylene, and acenaphthylene) have pyrolytic genesis, but various origins. For example, phenanthrene is mainly derived from combustion of coal and fossil fuels, while benzo(g,h,i)perylene and indenopyrene come mainly from combustion of gasoline in vehicles. Therefore, apparently, we have information about the pyrogenic sources of the PAH contamination.

There are stations with the indication on petrogenic PAH contamination (22, 32, 36, 42, 46) where fluoranthene/pyrene ratios were lower than 1.0. Recognising that these stations are widely geographically distributed, the existence of only one source of petrogenic PAH contamination is unlikely. Due to the absence of human settlements close to this stations it may be assumed that the petrogenic PAH contamination in sediments from these two stations is connected to shipping activity. All other stations characterised by high levels of pyrogenic PAH and probably connected with combination longrange transport of PAH and various local sources of pyrogenic PAH contamination (emissions from combustion of coal).

OC concentrations in bottom sediments from the Barents Sea are summarised in Table 2. OC residue levels in various stations is shown in Figures 5–8. HCB is a widespread contaminant that has entered the environment through its past manufacture and use as a pesticide and its

formation as a by-product during the production of a variety of chlorinated compounds. In aquatic systems, HCB is persistent in sediments and tends to accumulate in the tissues of organisms.

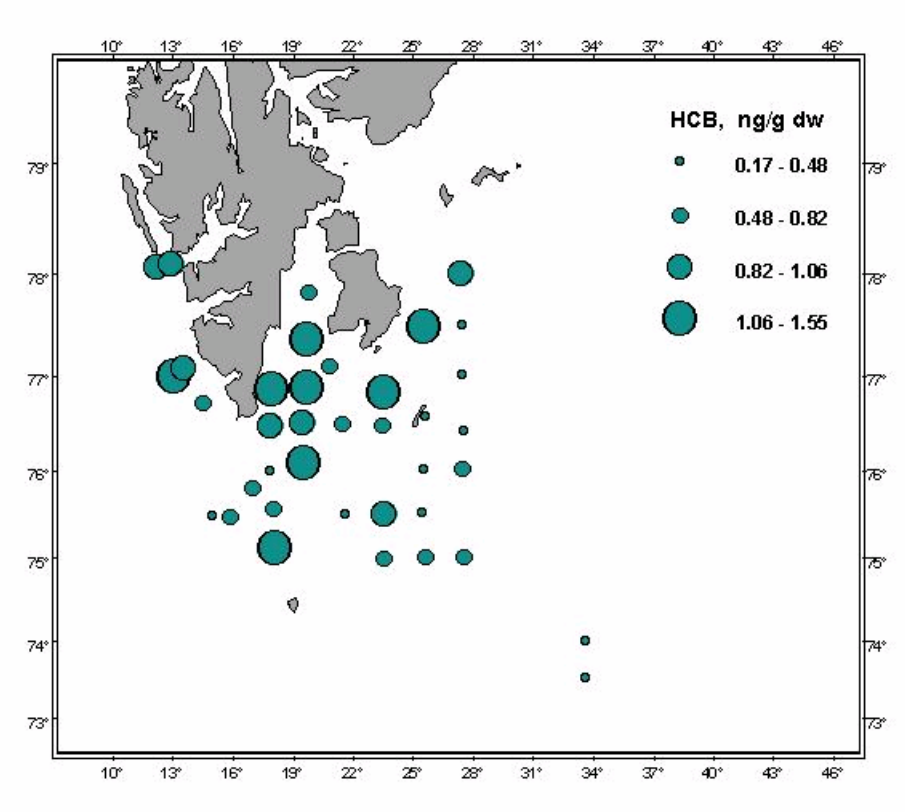

Figure 5. Content of HCB in bottom sediments from the Barents Sea (August-October 2005).

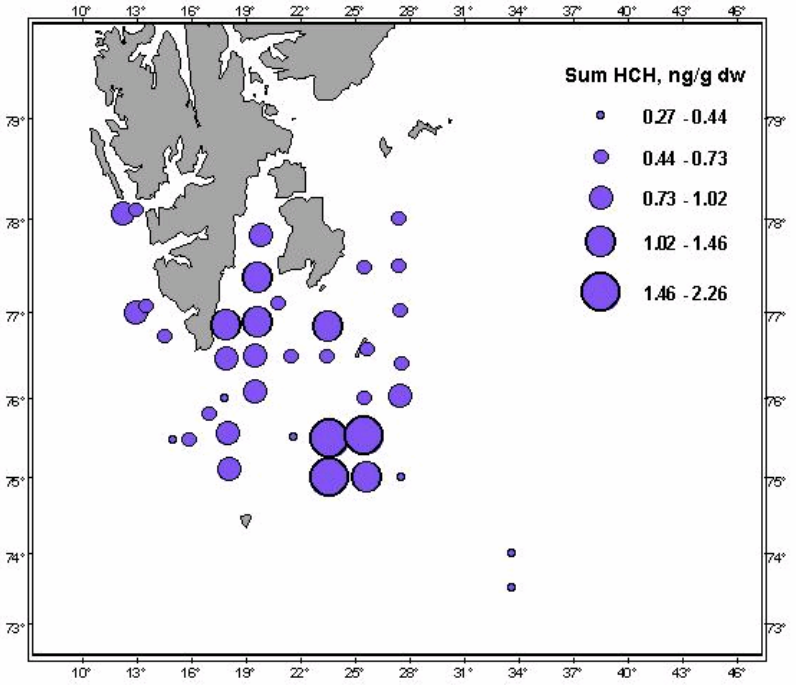

Figure 6. Content of HCH's in bottom sediments from the Barents Sea (August-October 2005).

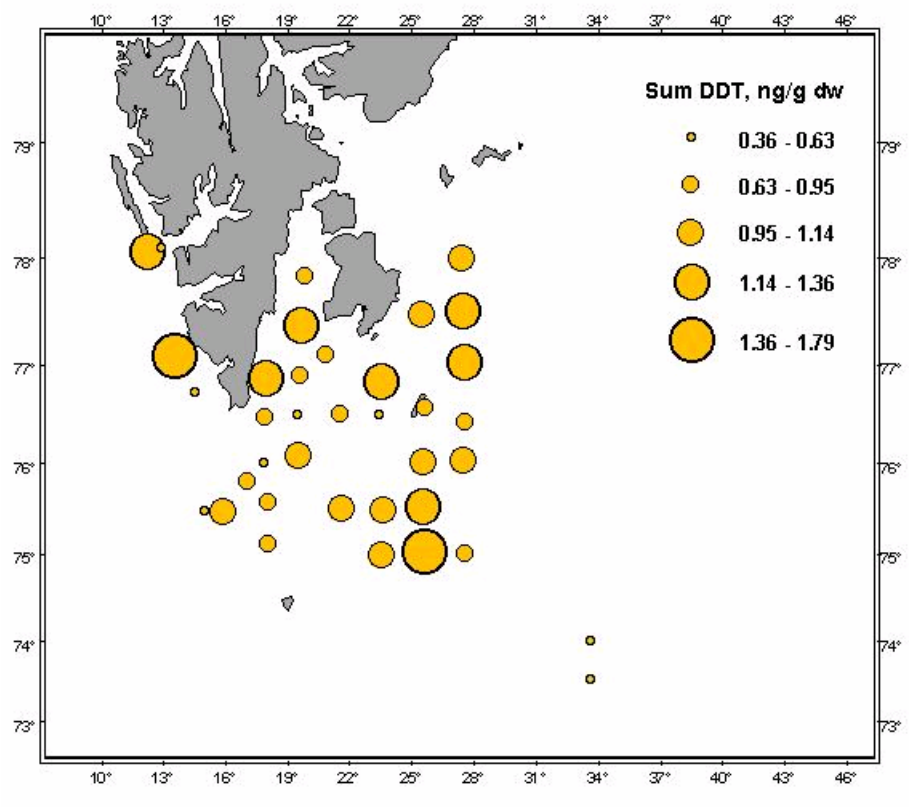

Figure 7. Content of DDT in bottom sediments from the Barents Sea (August-October 2005).

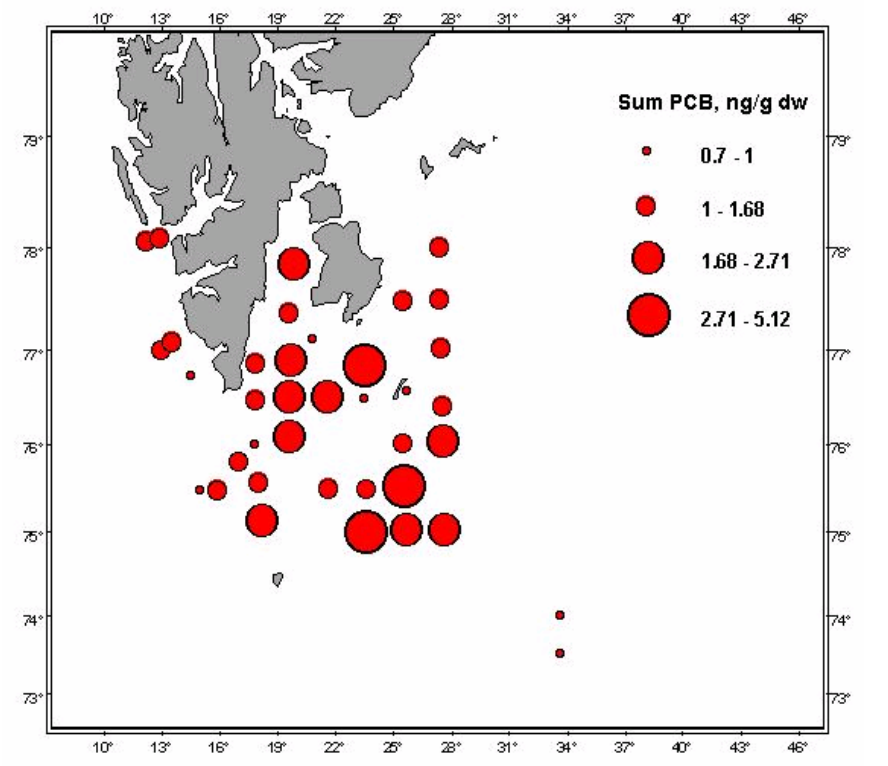

Figure 8. Content of PCB's in bottom sediments from the Barents Sea (August-October 2005).

HCB concentrations in all samples investigated were found to be in the range of 0.17–1.55 ng/g dry wt. (Table 2). Maximum HCB concentration was found at station 44 (Figure 5). HCB residue levels in bottom sediments of the eastern Arctic seas (Bering and Chukchi Seas and Gulf of Alaska), varied from 0.035 to 0.079 ng/g dry wt. HCB levels found in Barents Sea sediments were higher. However, it is known that in surface sediments from of Western Europe, the HCB concentrations can amount to 4 ng/g dry wt. (Northern Sea) and up to 6.7 ng/g dry wt., in harbours of northern Norway. Differences between HCB residue levels in Spitsbergen area sediments and sediments from other parts of Barents Sea (earlier obtained) were not significant. Elevated HCB levels in bottom sediments from Barents Sea are the result of long-range atmospheric transport.

Hexachlorocyclohexane (HCH) consists of mixture of four major isomers. The proportion of HCH isomers (α-, β-, γ- and δ-isomers) in the technical mixture varies. Pure insecticidal isomer, g-HCH, is called lindane. Lindane was used in Norway in the 1980s as an insecticide. In the Soviet Union, lindane (90% γ-HCH) was used instead of technical HCH. The former Soviet Union banned technical HCH in 1990. Differences between HCH levels measured in Barents Sea sediments were not significant for different stations, except stations 31, 32, 58. The sum of α- and γ-HCH in all sediment samples investigated ranged from 0.27 to 2.26 ng/g dry wt. (Figure 6). These levels were comparable with those in south-western and south-eastern parts of the Barents Sea 0.1–3.59 ng/g dry wt. and 0.1–2.88 ng/g dry wt. surface sediments respectively. While in surface sediment samples from the Chukchi Sea, Bering Sea and the Gulf of Alaska HCH levels were lower and ranged from 0.04 to 0.21 ng/g dry wt.

Concentrations of ∑DDT (sum of p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT and p,p'-DDT) varied not much (0.36–1.79 ng/g dry wt.) with the highest values close to Spitsbergen (Figure 7). Maximum ∑DDT was found in sediments from the stations 59 and high ∑DDT residue levels were detected at the stations 12 and 45 (1.58 and 1.36 ng/g dry wt., respectively). The average ∑DDT concentration calculated for north-west part Barents Sea sediments was, respectively, twice lower than those found in surface sediment from south-western part of the Barents Sea and approach to results from eastern parts of the Barents Sea. Residues of *p,p'*-DDT prevailed in all sediment samples with the exception of stations 31, 40 and 58. The *p,p'*-DDT/*p,p'*-DDE ratio (DDT/DDE) can be used to know whether DDT input occurs recently or in the past. Since *p,p'*-DDE is a dehydrochlorination product of *p,p'*-DDT resulting from the biological and photochemical transformation of the *p,p'*-DDT and not included in the technical DDT, higher and lower DDT/DDE ratios denote the recent and past usage of technical DDT, respectively. DDT/DDE is 1 in the atmosphere of high latitudes, and biotic and abiotic components of Arctic marine ecosystems. DDT/DDE ratio was found to range from 0.07 to 0.94 in surface sediments from the Barents Sea sediments. Both a low ∑DDT concentration and low DDT/DDE ratio indicate a not possible local DDT source in this area.

Concentrations of ∑PCB (sum of 12 congeners) in Barents Sea sediments had the higher levels than ∑DDT concentrations (Figure 8). Maximum ∑PCB residue level (5.12 ng/g dry wt.) was found in samples from station 58. The ∑PCB concentrations were somewhat lower at neighboring stations 31 and 59 (3.12 and 2.14 ng/g dry wt., respectively). The range of ∑PCB was lower than data obtained in the North Sea. The average ∑PCB concentration in Barents Sea sediments was same as found in surface sediments of the southwest and east parts of the Barents Sea. However, this value was significantly lower in comparison with those found in harbours of the northern Norway and Kola Bay. The PCB composition in sediment samples from the stations investigated differed. Low-chlorinated (tri-, tetra- and penta-) PCB congeners, accounted for 70% of ∑PCB, were predominant in sediments from station 15, 38 and 58. Along with penta-chlorinated PCBs, prevalent PCB homologues were high-chlorinated hexa- and hepta-PCBs (PCB-138, PCB-153 and PCB-180), accounted for more 55% of ∑PCB. There were not significant differences between absolute concentrations of penta-, hexa- and heptachlorinated PCBs in sediments from Barents Sea, and there were

insignificant differences between concentrations of tri- and tetra-chlorinated PCBs found in these survey locations. It is apparent that predominance of low-chlorinated PCB congeners in sediments from in most cases probably indicates that the main source of PCB residues is precipitation that is characteristic of unpolluted regions of Arctic. Due to the higher vapour pressure of low-chlorinated PCBs, they are subjected to atmospheric transport to a greater extent than higher-chlorinated PCBs.

Conclusions

i) The concentrations of PAHs and OCs in sediments from north-west part of the Barents Sea may be characterised as moderate, and comparable to the levels found in other open parts of the Barents Sea.

ii) Levels are higher than of the south-eastern Barents Sea and other offshore areas of the Arctic. The highest levels of contaminants were found southeast of Spitsbergen.

iii) The origin of both PAHs and OCs in the Barents Sea sediments is a combination of long-range transport from lower latitudes and local sources.

Annex 7: Review of the progress of the Passive Sampling Trial Survey (PSTS)

Note: Copy of this Annex is also included in the 2007 Report of MCWG

Presented by the PSTS Coordinating Group, WGMS/MCWG March 2007

1 Execution of the plan for the project

The joint session of WGMS and MCWG in 2006 developed the initial plan for the ICES Trial Survey and Intercalibration on Passive Sampling (PSTS). They also developed a timetable for the exercise. This is attached as Table 1, together with an additional column indicating the outturn dates for each step in the process. The exercise has been carried out and data are available for discussion at WGMS and MCWG in March 2007.

To summarise, the preparatory work to gain commitment from participants, prepare a protocol for the trial, prepare materials for deployment in the field, and distribute them to the laboratories closely followed the projected timetable. The final distribution of materials to participating laboratories was made on 29 September; only four days later than planned.

Deployment of samplers in the field was planned to begin in early October, but was delayed in some laboratories and was the last deployment occurred around 10 November. This delay was inevitably reflected in later aspects of the project, i.e. the sending of samples to the central laboratory for analysis, analyses in-house and by the central laboratory, and the reporting of data to the coordinator. Final samples for analysis were not received by the coordinator until March 2007 (target December 2006–January 2007). The coordinating laboratory will complete all outstanding analyses by the end of April. This date has also been agreed by the Steering Group as a deadline for the submission of in-house analytical data to the coordinator.

In total, 13 laboratories participated in PSTS, and sampling was undertaken at 31 locations for water and 25 locations for sediment.

Table 1. ICES Trial Survey and Intercalibration Passive Sampling, 2006-2007.

Initiative from WGMS and MCWG

PLANNING and OUTTURN TIMETABLE			
Activity	**Who**	**Planned Completion date**	**Actual Completion date**
Draft protocol for the experiment	Coordinating Group	May 2006	May
Get firm commitments from participants.	Coordinating Group and participants.	September	September
Determine degree of replication *	Coordinating Group	July	July
Confirm participants and locations	Participants / Coordinating Group	July	September
Draft Guidelines SEDIMENT	Coordinating Group	End of July	September
Purchase sampler sheets	RIKZ	June–August	June–August
Prepare and spike sampler sheets	RIKZ	August–September	August–September
Purchase of bottles	RIKZ	June–August	June–August
Prepare, spike bottles	RIKZ	August–September	August–September
Distribute bottles	RIKZ	September (25th)	September (29th)
Build frames to support samplers	RIKZ	July – mid September	July – mid September
Purchase mussels or use local animals	Participants	October	October
Distribute sample frames	RIKZ	September (25th)	September (29th)
Distribute sampler sheets	RIKZ	September (25th)	September (29th)
Deploy mussels, samplers and sediment	Participants	Early October.	5 October - 10 November
Record supporting data (CTD-data)	Participants	Simultaneous with the sampling	Simultaneous with the sampling
Recover mussels and samplers	Participants	Late November/early December	November - December
Shake sediment	Participants	October–November	?
Send sediment sampler bottles to central lab	Participants	December 06 - January 07	December 06 - March 07
Send sampler sheets to central lab	Participants	December 06 - January 07	December 06 - March 07
Analyses of samplers at central lab	RIKZ	Mid-January - February 07	December 06 - April 07
Complete analyses at local labs	Participants	Mid-January - February 07	January 07 - April 07
Send data to central lab	Participants	Early February	February 07 - April 07
Collate data	Foppe Smedes	End of February	March 07 - May 07
Review data	All	At WGs next year	March 07 and through to ASC 07

2 Issues arising in analysis of samples

2.1 Technical analytical problems associated with use of PRCs and other sources of problems

Several laboratories had reported difficulties during the analysis of passive samplers. In most cases, these were rather detailed points and varied between laboratories. The summary given here is a combination of comment from FRS (UK) and IFREMER (France). Information is being requested from other participants so that a wider view can be taken of the issues and that solutions can be developed that meet the needs of as many laboratories as possible.

2.1.1 Difficulties related to sampling:

- Filling of the coated bottle with the sediments slurry:
- Low dynamics of exchanges (Weak bottle shaking, weak water mass dynamics)
- Difficulties in estimating the sampling rate due to low water mass dynamics at the exposure site.

2.1.2 Difficulties encountered in the laboratory

2.1.2.1 Selection of Performance Reference Compounds (PRCs).

- Not all PRCs could be accurately determined with routinely used calibration standards. An accurate determination of PRC was not aimed because calculations of water concentrations are based on the relative loss of PRC. A reproducible determination of the PRCs was achieved in the silicone rubber before and after exposition with an modified adequat method.
- For the PCB PRCs we have to use an external calibration to quantify them as they are not part of the UKAS accredited method of the lab (we have identified the retention times and will be running such as soon as possible).

2.1.2.2 Extraction method:

- The main problem came from the use of a relatively large volume of MeOH for the cold extraction. All the analytical steps on the extract are routinely carried out in non-polar solvent. Therefore the exchange from the MeOH to non-polar solvent was necessary and required also a relatively large volume of intermediate solvent.

2.1.2.3 Interferences in analyses related to PRCs.

- Interferences of peaks (poor separation): Some of the PRCs are being used as internal standards (like d8-napthalene), which makes quantification of the PRC d8 naphthalene difficult. FRS does not use some of the PRCs (D12-phenanthrene, D12-perylene, D12-coronene, and all the CB PRCs), therefore, for the deuterated phenanthrene and Perylene, the calibration of their non-deuterated analogues were used to quantify them. The GC programme was not set up to look at coronene and therefore no result was presented. PCB 50 co-eluted with PCB 31 while PCB 104 co-eluted with a recovery standard (PCB 35).
- Interference PRC with standards (recovery, calibration, injection)
- Interference PRC with other contaminants:
- Only CB78 PRC could not be determined because of coelution on both analytical columns. The coelution problem for two other CB50 and CB204 PRC was overcome by the analysis on two analytical columns

2.1.2.4 General

- The most obvious issue is the differences in analytical procedure for extraction, clean-up, and quantification. We split the extracts into two (PAHs and PCBs) and the PAHs were cleaned up using the HPLC (silica column), while the PCBs are to be

cleaned up with Alumina column. The PAHs were analysed by GC MS and the PCBs using GC ECD.

2.2 Evidence of gross contamination of samplers

Gross contamination of samplers is most likely to arise through mis-handling of sheets used for water sampling, or contamination of films on sediment sampling bottles during preparation or distribution.

Some sheets and bottles were spiked with Performance Reference Compounds and distributed to participants. These were not used for field exposures or sediment extractions, but were returned to the central laboratory for analyses. These analyses showed no evidence of gross contamination and therefore gross contamination during preparation or transport of rubbers is considered unlikely.

It is possible that contamination could occur during field deployment and recovery of PS material. To attempt to limit the probability of this occurring, the exercise protocol contained detailed advice on how to handle the PS materials.

There is no evidence in the analytical data from the central laboratory to suggest that the samplers became grossly contaminated during the transport and handling necessary for their use in the field. The correlations observed between the results for water samplers and for those in sediment at the same sites indicate that gross contamination could not have frequently occurred. In a few cases, the concentrations of some PRCs in the water samplers appeared higher than might be expected from the data for other PRCs in the same sampler. This mainly occurred in samplers deployed at heavily contaminated sites. It is possible that in such circumstances the concentrations of contaminants in the environment and consequently absorbed by the PS were sufficiently high to interfere with the measurements of the residual concentrations of some PRCs in the samplers.

2.3 Are the values for the partition coefficients satisfactory?

Accurate values for partition coefficients of contaminants between PS materials and water are necessary for the calculation of concentrations of contaminants in both water and pore water. Values for some partition coefficients are available in the grey literature. The central laboratory has put considerable effort into the determination of partition coefficients for a range of PS materials, including the material used in the water sampling sheets and that used in the sediment sampling films. The values obtained from direct partitioning between water and passive sampling material are consistent with those obtained by extrapolation of coefficients obtained from a series of water/methanol mixtures and are considered to be reliable to within <0.05 log units.

The difference between the sets of partition coefficients for the two different PS materials used in sheets and in films is small (<0.1 log units), and calculations by the central laboratory have been based upon the mean of the two sets of data. These means were distributed to the participating laboratories for use in their own calculations.

2.4 Discussion of model of sampling rates

It is necessary to estimate sampling rates of PS in water in order to calculate the concentrations of contaminants in the water phase. PRCs (PAHs and CBs) are added to sampler prior to exposure, and the dissipation rates of the PRCs are used to estimate the sampling rate. The protocol for the PSTS instructed participants that they should only use PRCs for which the retained amounts were greater than 10x the detection limit, and less than 50% of the initial amount added to the sheets. Sampling rates should be calculated for each PRC that met these criteria, and then the median value used as the best estimate of the sampling rate.

In practice, this caused some participants some difficulties. For example,

a) Some PRCs interfered with other compounds in the analyses, for example with analytes, internal standards or recovery standards

b) Some PRCs were not covered by the normal instrument method used

c) PAHs and CBs could be analysed separately, thereby reducing the number of PRCs available for the estimation of sampling rate

d) In some cases, only a small number of PRCs met the acceptability criteria listed above

e) In some heavily contaminated areas, there is greater possibility of interfering compounds being present which co-elute with the PRCs, and this can be difficult to recognise.

f) Estimates of sampling rates derived from different compounds could be rather different, for example as a result of e) above.

In recognition of these sources of uncertainty, an alternative improved method of handling the PRC data has been applied by the central laboratory to their own data (and will be applied to the raw data provided by participating laboratories).

The loss of PRCs is modelled as a function of a set sampling rate. By using Excel solver, the sampling rate is optimised to minimise the sum of the squares of the differences between the observed and modelled values. Deviations from the fitted model are normalised to an estimate of the measurement error in the observed values.

The modelling uses data for all PRCs for which the remaining amount is between 1% and 90% of the original amount added to the sampler. Outliers arising from processes such as those described in a) – f) above can be easily recognised and assessed for their effect on the modelled sampling rate.

2.5 What physical problems and difficulties have we seen?

In general, few practical problems were encountered during the exercise. Problems with potential differences in the interpretation of the protocol were largely eliminated by the text being reviewing by more than one person. However, a very few misunderstandings still occurred and the protocol for any future exercise will take these into account.

Only one instance of loss of water samplers was reported. This occurred in the Seine estuary after a storm, despite being attached a 2 tonne flotation buoy. The buoy was recovered from a beach, but the samplers were lost.

Some damage occurred to sampling films in 4 (20%) of the sediment sampling bottles. Loss of film can be detected either visually, and by the routine weighing the bottles at the end of the process. This procedure can be confounded if the glass of the bottle is chipped, as weighing cannot distinguish between loss of film and loss of glass.

Damage/loss of PS films is normally associated with extraction of sandy sediments, which act as an abrasive over the extraction period. This can be greatly reduced by avoiding the use of sandy sediments. There may also be some potential for improving the adherence of the PS film to the glass surface of the sampling bottle, or for different methods to detect abrasion of films.

2.6 Influence of biofouling

Some participants experience very heavy growth of fouling organisms on both the frames and sampler sheets deployed in the water. Fouling was particularly heavy at the two stations in Brisbane, Australia and at one station close to Vigo, Spain.

It is likely that this has had only limited impact on the data. Firstly, it is unlikely that the fouling will have significantly reduced the transport of contaminants to the sampler. The rate of transport is the product of the solubility of the material and its diffusion coefficient in the material being considered. The solubility of contaminants will be greater in the fouling organisms than in water by a factor equal to the bioaccumulation factor, and the diffusion coefficient is unlikely to be reduced to the same extent. Therefore, the rate of transport is unlikely to be greatly reduced by the presence of fouling organisms. In addition, the PRCs added to the samplers act as a control for the rate of sampling and should reflect any changes in the sampling rate induced by the presence of the fouling communities (Booij, 2005).

2.7 Influence of low sampling rates on detectable residues and hence on confidence of concentrations in water

One important advantage of passive samplers is that they continue to sample water over long periods of time, and thereby both integrate over time and also accumulate contaminants from relatively large volumes of water. For example, sampling rates in the current experiment for deployments of sets of 6 sheets were typically 5 – 40 litres per day, giving a total volume sampled over a deployment for 40 days of 200 – 1600 litres. These very large volumes allow the estimation of rather low concentrations of dissolved contaminant in the pg/l range, using commonly-available instrumentation for detection of the analytes.

The effective sampling rate is strongly increases linearly with the surface area of the sheets deployed and the flow rate of water past the sampler (which controls the thickness of the diffusive boundary layer around the sampler). Clearly, if the effective sampling rate, and hence the total volume sampled is reduced, for example by deployment of a smaller number of sheets, the lowest detectable concentrations will increase by an equivalent factor.

Similarly, deployment of samplers in areas where water movements are not strong also reduces the volume sampled. For example, Loch Etive is a very sheltered fjordic inlet in the west of Scotland and the effective rate of sampling at this point was 3.6 litres per day. This problem can be very significant in quiescent waters, such as in lakes, but is normally less important in estuaries and the open sea where tidal and other currents ensure that water flows past the samplers.

A potential significant improvement in the capability of passive samplers in water would be a system to keep the sampler sheet in motion (e.g. spinning) for several weeks of deployment. However, the energy required for this is significant and systems have yet to be developed.

3 General comments on results obtained up to March 2007

The objectives of the PSTS project were:

a) to extend the geographical range of the validation of the use of passive samplers in water,

b) to transfer knowledge of the methods more widely within the ICES community,

c) to gain experience in the use of passive samplers,

d) to estimate the contribution of the analytical component to total variability,

e) to gain further information towards the validation of passive samplers in sediment.

Even at this early stage in the collation and interpretation of the results from the project, it is clear that objectives b) and c) have been met. Thirteen laboratories have participated in the trial. In addition, passive samplers have been used in new areas such as Faroe, Ireland, Spain and Portugal that are distant from the original uses of silicone rubber samplers in the Netherlands.

Some other objectives cannot yet be addressed until the data set is more complete. For example, the low numbers of data on mussels and worms have delayed consideration of the relations between residues in organisms and concentrations detected by passive samplers. These matters will be addressed as the data become available.

However, the datasets for samplers analysed by the central laboratory, while not complete, is at a stage where some preliminary observations can be made as to whether the data are reasonable in terms of our understanding of inputs of contaminants and of environmental processes affecting their behaviour.

The following bulleted points are preliminary observations on the distribution maps of concentrations of contaminants (PAHs, CBs, HCB) in water and in sediment pore waters.

3.1 Water

PAH

- For all PAHs, the concentrations in Norwegian samples are very much higher than all other locations. This may reflect the source from aqueous discharges, particularly of heavier compounds, from aluminium smelters.
- There is a tendency for concentrations in far west stations (Scotland, Ireland, Faroe) to be as high as those in areas of the SE North Sea where concentrations might be expected to be higher. This could reflect high concentrations of SPM in the North Sea adsorbing PAHs and reducing the free concentrations, whereas atmospheric inputs in the west occur into water with low SPM and therefore higher concentrations may remain in solution.
- In the outer parts of the Scheldt, concentrations of lighter PAHs increase seawards, This could also be a result of dominating atmospheric input. Alternatively degradation of organic matter cause PAHs to desorb from the solids. This likely not the main reason as this increase seawards is not present for heavier compounds.

CBs

- CB concentrations at sampling stations in Norway and western locations (e.g.Scotland, Ireland, Faroe) are all low. There are no large local inputs, and no significant atmospheric inputs, in these areas.
- The high concentrations in the inner Scheldt decrease seawards. This could reflect dilution of river water by open sea water and lack of desorption of CBs from suspended solids.
- Concentrations of more chlorinated CBs are relatively dominating in Vigo, Spain.

HCB

One very high concentration of HCB was found in the Elbe. Apart from that, there is a tendency for higher concentrations in western parts of the survey area, particularly in Faroe. This may reflect atmospheric transport and deposition in areas of low SPM.

3.2 Sediment pore water

PAH

- Concentrations are generally high at stations in Norway. The pattern is more pronounced for heavier compounds (e.g. Indeno(1,2,3-cd)pyrene, Benzo(ghI)perylene, Benzo(a)pyrene, Benz(a)anthracene), possibly reflecting sources of heavy PAHs from aluminium smelters.

- There is a tendency for higher concentrations of lighter compounds (e.g. Acenaphtene, Fluorene) in areas likely to receive petrogenic inputs, such as Aberdeen harbour and Scheldt (Antwerp).
- In the Scheldt area, concentrations generally decrease in a westerly direction out of the estuary and away from river inputs

CBs

- There are high concentrations in the Seine and Scheldt estuaries, where it is known that inputs occur.
- Concentrations in Norway and Scotland are low, and these areas are likely to be remote from inputs.
- The relative concentrations in Vigo, Spain increase with increasing degree of chlorination (44, 101, 153, 187,).

HCB

- HCB is prominent in 1 out of 2 samples from the Kiel area, and low in Western Scotland and Portugal.

4 Further work on PSTS and other perspectives for the future

As discussed earlier, the full set of data for PSTS is not yet available. The target is to complete all analyses and for them to be submitted to the central laboratory by the end of April. Once this has been completed it will be possible to address outstanding aspects of the objectives, including:

- Intercomparisons between laboratories
- Validation of the water sampling through combination of analyses of mussels and PS in water
- Validation of the pore water (sediment) sampling through combination of analyses of worms and PS in sediment
- More complete sets of field data and more detailed interpretation of the field data
- Comparisons of water and pore water analyses from the same location.

Opportunities will be sought to communicate the results more widely. Firstly, Theme Session J at the ICES ASC07 is concerned with the application of passive samplers and it is hoped that several papers will be presented in PSTS. Publication in the open literature will also be an objective.

Already it is possible to see some themes emerging from the practical experience gained through PSTS. Firstly, the selection of PRCs is very important. They must cover the necessary range of K_{OW} values, be compatible with routine analytical procedures for target contaminants (such as CBs and PAHs), not degrade during the exposure period, and not be found in the environment. Individual laboratories have additional factors to consider, such as avoidance of interference with internal standards or recovery standards. Analytical comments of this type will be collated and reviewed when all data have been received.

One of the difficulties encountered is the low rate of sampling (as low as 3 litres per day) at some sampling points where water movements are weak. Weak currents result in a relatively thick diffusive boundary layer around the PS, and reduce the rate of transfer of contaminants to the PS. If it was possible to artificially maintain the sampler in motion (e.g. spin a disk of rubber) this could reduce the problem. However, so far the energy requirements for this have not been solved.

Silicone rubber PS are not particularly suitable for more polar compounds. Other materials may be more suitable, but in many cases it may be simpler to analyse the water directly as the compounds will partition more strongly into the water phase than, say, CBs or PAHs.

It is now necessary to seek other opportunities for the application and development of passive sampling. Some national projects are emerging that use passive samplers, and this is to be encouraged. In addition, the proposed NSHealth/ICON project might be a vehicle for quite widespread deployment of passive samplers over the OSPAR area.

OSPAR has so far paid relatively little attention to water sampling in its monitoring and assessment activities. Poor detection limits in relation to environmental concentrations, high inter-sample variability of water samples, and the inability of water analyses to reflect the pollution hazard presented by contaminants in water were significant considerations in OSPAR decisions to concentrate contaminants monitoring on sediment and biota as being at the time a more effective approach to monitoring the consequences of control measures. Passive sampling holds out the prospects that these difficulties may now be less significant and it may be that the previous decisions could be reviewed in the light of OSPAR long term objectives for contaminants in the marine environment.

Normalisation of contaminant concentrations in sediments has been used to reduce the influence of gross changes in sediment composition between samples and sites, in the hope that polluted sediments might be more clearly recognized. The application of passive sampling of sediments directly addresses the potential biological impact of contaminated sediments and therefore opens new opportunities in the assessment of sediment quality.

Other possible areas of application include the EU Water Framework Directive and the emerging Marine Strategy Directive.

Annex 8: Publication list from Lancaster University concerning passive sampling (DET, DGT) for metals and other hydrophilic substances

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Annex 9: Guidelines on the use of passive samplers in sediment

Draft Guidelines for *In-Vitro* Passive Sampling of Sediments using silicone rubber in sheet or film form

1 Introduction

1.1 Objective

The purpose of passive sampling of sediments is to estimate the free dissolved concentrations of contaminants that would be in equilibrium with the sediment. This is essentially equivalent to the free dissolved concentrations of the contaminants in the pore-water. The method described here applies to hydrophobic compounds such as CBs, PAHs, with $\log K_{OW}$ values between 3 and 8. As the "passive sampling" is done in the laboratory, it is referred to as "*In-Vitro* Passive Sampling"

1.2 Principle and theory

A reference phase with a known reference phase-water partition coefficient (K_{RW}) is brought in contact with a large amount of sediment in the presence of sufficient water to make the mixture fluid. The system is closed and then shaken, tumbled or otherwise agitated to obtain an equilibrium partitioning of contaminants between the sediment and the reference phase. By measuring the concentration in the reference phase (C_R), the free dissolved concentration in the water phase (C_w) can be calculated using the K_{SW}

$$C_W = \frac{C_R}{K_{SW}}$$

The estimate of the free dissolved concentration in the aqueous phase (pore water) is approached more closely if the capacity ratio between the sampler and the sediment is as low as possible, i.e. a large amount of sediment is equilibrated with a minimal amount of the reference phase. The capacity ratio can be monitored by the addition of performance reference compounds (PRCs) to the reference phase prior to exposure. Characteristics of suitable candidates for PRCs are discussed, and examples given, in Annex B. During exposure (equilibration), the PRCs will distribute between sediment and reference phase according the capacity ratio. If less than 10% of the added PRC has remained in the reference phase, then the original free dissolved concentration is also determined to within 10%, which is generally sufficiently precise, for example for comparison with concentrations in local biota. By PRCs covering a range of different hydrophobicity (e.g. CB10, CB50, CB104, CB145 and CB204) a similar distribution between the two phases is an indication of equilibrium. The latter compounds, with higher Kow values, will require more time to attain equilibrium. It should be noted that equal distribution should not be expected for different PAHs (deuterated) used as PRC. PAHs are subject to other sorption mechanisms in addition to purely hydrophobic partitioning into sediment. Higher PAHs show greater sorption to sediment than to the hydrophobic reference phases.

1.3 Criteria for the selection of a passive sampling reference phase

Many hydrophobic plastics have been considered for use as reference phases in passive sampling, with polyethylene (PE), polyoxymethylate (POM) and silicone rubber (such as polydimethylsiloxane, PDMS) being the most frequently used. Material for use as a reference phase should have an open structure and a transport resistance to the target contaminants that is less than that of water, so that the transport of compounds within the sampler does not limit

the uptake rate (Huckins *et al*., 2006). Soft materials like PDMS and PE fit these criteria better than hard plastics like POM (Rusina *et al*., 2007). POM does not have an open structure and has negligible permeability, and consequently long equilibrium times (Sungwoo *et al.,* 2005). If the material has a closed structure, the sorption of contaminants relies only on surface effects. If the affinity of such a reference phase for contaminants is similar to that of biological material, the biolayer that inevitably forms on the surface of samplers deployed in the field could easily dominate the uptake by the sample.

To achieve equilibrium in the shortest time, the reference material should be as thin as possible. The lower limit to the thickness of samplers is mainly determined by practical limitations in handling very thin materials. Additionally, a minimum amount of reference phase (e.g. 0.3–0.5 g for silicone rubber) is required to collect sufficient quantities of the contaminants for subsequent analysis. Thin sheets with a large surface would be ideal, and sheets of around 0.5 mm thickness are robust and easily handled. Much thinner sheets are difficult to handle, and can be easily torn. Very thin layers require support from dome other material, and a particularly effective way to do this is by coating a layer of silicone rubber onto the inside wall of a glass bottle. Thickness of the film can be as low as 10µm and about 0.4 g of rubber is required to coat the inside of a 1 liter bottle. After precleaning, the film can be equilibrated with up to about 400g (dry weight) of sediment.

2 Sediment sample and sampling

Sediment samples can be taken according to the OSPAR guidelines. The nature of the method described here is such that some disturbance of the surface layer, and perhaps some consequent loss of fine material, is not critical for the outcome of the measurement.

In general, at least 0.5 litre of sediment suspension is required for a single determination. Considering the relatively large weight of sample required for one measurement, homogenisation of the bulk sample is not critical and simple manual stirring will generally be sufficient. The use of very sandy sediments (organic carbon content less then around 1%) is not advisable, because:

(1) the capacity of the sediment is very small and may be insufficient to equilibrate with the reference phase without deviating significantly from the original pore water concentrations, and

(2) sand works as an abrasive during the equilibration period and can damage the thin layer of sampler on the inside of the bottle.

Samples should be stored cool (4°C). Long storage times (over 6 weeks) are not recommended but so far no comprehensive investigation has been undertaken to quantify any possible effects. Similarly, the effects of freezing on sorption properties has not been established.

3 Material preparation

3.1 Sheet material

Reference material obtained in sheet form should be cut into appropriate sizes. Typically, 0.3-0.8 g as sheet or coating is required for 0.5 kg dry weight of sediment. Details of the method for coating bottles are given in Annex A.

New sheet material must be pre-extracted to remove any contaminants that may be present and also to remove oligomers (low molecular weight polymers). This is done by soxhlet extraction for 100 hours with ethyl acetate. A large size soxhlet apparatus that can contain several pieces of cut sheet is convenient for this process. Only 30% of the soxhlet volume may be filled with sheets to allow space for the sheets to swell as they absorb the solvent. Alternatively, sheets

can be shaken with ethyl acetate (20 ml/piece) for one week, refreshing the ethyl acetate twice during that period. The completeness of the extraction process can be measured by determining the non-volatile mass in the last extract of the sheets. After extraction, the sheets are dried in a fume hood and transferred to a wide mouth glass bottle with methanol and shaken overnight. The methanol extracts any contaminants sorbed during the air drying process. Pre-cleaned sheets can be stored under methanol for a prolonged period.

It is recommended to use dedicated or disposable glassware for solvent containing residues of oligomers of polymeric material. Oligomer residues disturb the GC process and block HPLC instruments. This glassware should therefore never be used in the analytical processes. It is difficult to clean as residues only dissolve in "hot" ethyl acetate. However, this indicates that soxhlet equipment used for pre-cleaning will not be contaminated.

3.2 Bottles

It is necessary to keep track of the weight of the coating in bottles used for equilibration. Therefore, no labels should be used on the coated bottles and bottles are weighted without cap. Bottles can be marked by engraving a number or a letter and a number, and it is advisable to develop a bottle dictionary in which the weights of bottles during use are recorded. The weights of engraved empty bottles should be recorded to 0.001 g without cap. Accidental exchange of caps will cause errors in weight.

Coated bottles used should have an air and liquid tight closure using an aluminium lined insert in the cap. This is more easy achievable for bottles with a small neck diameter. Coverage of the liner in the cap with aluminium foil is essential as any plastic cap will also act as a passive sampler. Adhesive Aluminium foil tape (Tesa) stuck to a semi-soft (PE, Teflon will do) liner can be used.

This system is sufficiently watertight but cannot withstand pressure. Therefore before horizontal shaking with solvents a period of acclimatisation (equilibration between solvent and overlaying air phase) and subsequent release of pressure is required. A more secure way is to acclimatise at a higher temperature than that at which the shaking process is to be performed, and in that way the inside of the bottle will be at a slightly lower pressure than the ambient atmosphere. Alternatively, extraction with solvents can be performed on a roller, provided that the whole film is wetted sufficiently by the solvent.

Before use, bottles should be shaken three times for 24 hr with 50 ml ethylacetate. To reduce the amount of solvent used, a second extract aliquot can be used for a first extraction of the next bottle, and the third for a second extraction, etc. After extraction, bottles are dried in a flow of nitrogen in a fume hood, weighed, and the final film weight is determined. Closed with a cap as described above, the bottle can be stored in this condition.

4 Spiking with Performance Reference Compounds, blanks and storage

4.1 Individual spiking

Pre-extracted sheets are taken from the methanol and wiped with a tissue. Spiking of PDMS sheets that easily take up solvents can be done by simply dosing the PRC solution onto the individual sheets and let the solvent evaporate. Completeness of evaporation can be checked by weighing. The PRC concentration should be such that no more than 10-20% of the sheet weight is added as spike (i.e. a spike volume of around 50µl is suitable). Bottles are spiked in a similar way by dosing the PRC solution directly onto the film. At least two bottles, or one out of every 10 bottles, which ever is the greater number, are used as reference samples and

are analysed without exposure to sediment. Bottles can be stored in the freezer for at least half a year

4.2 Batch spiking

A batch spiking procedure can be applied to all types of sheets, including those that do not easily sorb solvents (Booij *et al*., 2002). The methanol in which the batch of sheets (10-100) is stored can be poured off and 80% (v/v) methanol/water is added, up to a maximum of 4 ml per g of sheet. The PRC spiking solution is added to this mixture and the mixture shaken or tumbled overnight. Then 2 ml water per sheet is added and the mixture is shaken or tumbled for 48 hours. The sheets will have taken up the PRCs according to their sorption capacity (i.e. proportional to their weight). Sheets can be stored like this for at least half a year in a freezer and be used for exposure to sediment when appropriate. During the analysis of sheets after exposure, at least two non-exposed sheets should be extracted and analysed in parallel for reference in each exposure experiment.

4.3 Amounts for spiking

In the ideal situation, the PRCs are entirely transferred to the sediment and not detectable in the film. To ascertain that at least 90% has dissipated from the film, 10% of the added amount has to result in a signal above detection limit. However in samples co-eluting or closely eluting compounds may disturb proper quantification and a higher amount of PRC is appropriate. Practical amounts range from 100–1000 ng per sampler.

5 Exposure to sediment

Coated bottles prepared and spiked with PRCs at least 48 hr before use, or uncoated bottles (with caps) for later addition of a spiked sheet, are weighed. Then about 0.5 – 0.7 kg (0.5 L) of homogenised wet sediment sample is transferred to the bottle. If thought necessary, mechanical homogenisation can be undertaken using a spiral paint mixer or equivalent. Some water may be added to liquefy the sample prior to homogenisation, and for convenience when filling the bottles. The sample weight is recorded and, in parallel, dry weight determination is performed on a subsample to allow determination the actual dry weight of sediment being equilibrated with the sampler. Some additional water (record the amount) may be added to liquefy the sample further to improve the shaking. However, excessive dilution will decrease the uptake and equilibration rates. About 80% water content is necessary to suspend clay materials, whereas sandy material already "fluidises" at 25–30% water content. Note that sandy material is difficult to shake as it quickly settles out of suspension into a solid phase. The spiked sheets are then added to uncoated bottles.

Before beginning the equilibration process, the bottles are purged with nitrogen to remove as much as oxygen possible. Then the bottles, with sediment, are placed on a shaker at a speed that keeps the sediment in suspension. In general, an orbital shaker at 125 rpm with an amplitude of around 3 cm will do the job. Tumbling or rolling can also be used, but show exchange rates that are lower by a factor of about 2. The range of equilibrated compounds is extended to those with higher hydrophobicity by:

- longer shaking period;
- higher surface area-volume ratio of the sampler;
- higher concentration of solids in suspension (i.e. clay/water ratio);
- lower average particle size;
- and higher shaking intensity.

Experience indicates that minimum conditions with a 5x5x0.05 cm sheet (50cm^2) will require about 2 weeks for equilibrium to be achieved for compounds up to logK_{OW}≈5-6. So far, a

maximal situation occurs in a bottle coated with a 10µm film with a muddy suspension which in 3 weeks will equilibrate for compounds up to logK_{OW}≈7-8 (i.e. covering all "routine" PCBs and PAHs). Whatever shaking conditions are available, a shaking time of 3 weeks is suggested. It may be that an improved approach may become developed later. Shaking should be done in the dark and preferably at 20°C.

After shaking, coated bottles are emptied and quickly rinsed with 1–3 small portions of water (±50 ml) to remove residual sediment. As much residual water as possible is removed by shaking/swinging the bottle. At this point, an analytical recovery standard can be added.

Sheets can be recovered from the sediment, washed with little water, wiped with a tissue and stored in a small sealed glass container with aluminium foil lined cap. Analytical recovery standard can be spiked on the sheet at this point.

Sealed bottles or vials can be stored in the freezer until extraction and analysis.

6 Extraction and cleanup

6.1 Solvents

To prevent damage to sheets and coatings, extraction is better carried out using a solvent that does not cause a large degree of swelling in the sampler, and is not able to extract any possible residual unpolymerised material from the rubber. Depending on the type of sheet used, different ranges of solvents can be applied. Materials used for passive sampling do generally not have very strong sorption properties. The material-methanol partition coefficient, K_{mm} is less than 1 (log K_{mm}=0) (Booij *et al*., 2002) for all compounds up to logK_{OW}<8, and therefore methanol an appropriate extraction solvent. Less appropriate alternatives are ethanol (high boiling point) or acetone (possible radical formation that degrades PAHs). A very good alternative is acetonitrile, as, unlike acetone, it shows no degradation. The 15% azeotrope with water also guarantees a dry extract after evaporation. However, acetonitrile is considered rather toxic and the boiling point is quite high. For silicone rubber materials, methanol is presently the best choice. A wider range of solvents, including pentane, can be used for extraction of PE and POM.

6.2 Extraction

The small mass of the film or sheet sampler (<0.8 g) allows quantitative extraction of the target contaminants with only small amounts of solvent. Coated bottles can be extracted twice with 40 ml methanol, shaking each time for 2 hours. Sheets up to 1 g (≤0.5mm thickness) can be extracted twice with 20 ml methanol and 4 hours shaking time. The extraction time for sheets is related to diffusion of compounds from the inside of the material and consequently increases with the film/sheet thickness.

As noted above, the alufoil-lined caps are not pressure tight. Before horizontal.shaking, the bottles should be equilibrated so that no pressure builds up during shaking. Warming the bottle in hot water before closing will create a partial vacuum in the bottle during the extraction. If the sheet in the vial is completely immersed in solvent, the extraction vial can be shaken upright. Alternatively soxhlet (or even ASE extraction) can perhaps be applied to extract sheets only. Weighing the bottle or flask before and after extraction may indicate solvent losses.

Combined extracts are transferred to an evaporation flask and on a waterbath and evaporated using Kuderna Danish apparatus or equivalent equipment to 1–2 ml.

Extracted bottles are dried and weighed, the weight registered in the bottle dictionary, and the film weight calculated. Sheets are dried and the weight recorded.

6.3 Cleanup

All cleanup steps that are routinely applied to sediment extracts for determination of contaminant concentrations can also be applied to extracts from passive samplers. Compared to sediment extracts obtained by solvent extraction, an extract from passive sampling generally contains a very low amount of matrix material, and even direct analysis without clean-up can be considered. For accurate analyses at trace level, a cleanup is probably required. Additionally, it is possible that incomplete pre-extraction of sampling material may result in small amounts of oligomers being present in the sample. The non-specific cleanup described below will remove this material, together with all other highly hydrophobic material (which is often high molecular weight and including lipids).

Starting with an extract in methanol, a non-specific cleanup can be conveniently carried out using a C18 bonded silica cleanup. A glass cartridge with 500mg C18 bonded silica is pre-eluted with 10 ml methanol. Then the extract is transferred to the cartridge, washed down and eluted with methanol. The amount of methanol needed for elution is around 6-10 ml, but an elution test should determine the volume required for the target contaminants. Instead of methanol, acetonitril can be applied, and has been found to elute faster because of its lower viscosity. This cleanup isolates all, and only, compounds up to $\log K_{OW} \approx 9$, i.e. a wide range of environmental contaminants, including CBs and "routine" PAHs. Alternatively, GPC fractionation can be applied to obtain a similar cleanup.

After this non-specific cleanup, a further specific cleanup can be applied. This will depend on the target compounds and instrumental method applied. This may include removal of sulphur, e.g. by addition of copper powder and ultrasonic treatment.

6.4 Concentration

The low matrix content increases the risk of losses of target compounds through volatilisation as a high matrix can act as a "keeper". Extra care in concentrating sample extracts is required and evaporation to dryness should be avoided under all circumstances. Distilling evaporation systems include some plates for separation, and are preferred over rotavapor or (automated) systems that use a nitrogen flow. The latter do not have a reflux flow that can extract the target compounds back from the vapour stream. Considering the small amount of solvent, a miniature Kuderna Danish apparatus with one Snyder ball is optimal for providing in 1-2 ml extract after evaporation. To evaporate methanol, a water bath at about 95°C is required. Whatever system is used should be checked for its performance with the solvent-target compound combination of interest.

6.5 Phase transfer

As evaporation to dryness causes losses, solvent transfer should be performed in a way that avoids complete evaporation. The simplest way is to take advantage of azeotropes. An extract of 1 ml methanol or acetonitril is transferred to hexane by adding 10 ml hexane and subsequently evaporate again to 1 ml using Kuderna Danish distillation. The azeotrope (methanol/hexane 1+3) boils at 50°C and with excess hexane the evaporation will result in a solution of the analytes in hexane. Note that hexane and methanol are not miscible. Similarly, transfer from hexane to methanol can also be performed without the necessity of evaporation to dryness.

Application of azeotropes for phase transfer can only be used when the solvent is evaporated through a distillation process. Nitrogen blow down systems will only evaporate the upper layer (i.e. hexane). In those cases, a solvent extraction will have to be performed. After dilution of the methanol with water (5 ml water for each ml methanol phase) the target compounds can be extracted twice with 20 ml pentane or hexane.

7 Analytical QA

Analytical QA focuses on the process of analysis of the target compounds held in a coated bottle or sheet. This is equivalent to the approach taken in the analysis of any other environmental matrix.

1) By executing the extraction procedure without sample, the blank values are determined. Some blank values of lighter PAHs seem to be inevitable, but at the same time these compounds generally give the highest signal in PS sampling. The procedural blank can be subtracted from the results.

2) Analysing reference sheet/bottles in duplicate will give a more reliable value for the initial concentrations of the PRCs, as well as some information on the repeatability of the analysis. The reference sheets/bottles should not contain any of the target analytes and indicate a maximal blank value. This should not be subtracted from sample results as these compounds take part in the equilibration process and only need consideration if there was sufficient present to seriously increase the amount of contaminants in the whole system.

3) To monitor the recovery of the analytical procedure for individual analytes, one or more recovery standards can be added from the start of the analyses, as indicates in the text above. Comparing nominal values with measured values will indicate the recovery. Values should be over 80%.

Formal QA, and laboratory performance studies, for passive sampling are still under development. Sheets or bottles containing known concentrations of analytes to use as reference material may become available in future. Intercalibrations may help to further improve the methods and increase robustness. Also validation by using different materials, conditions, and methods should be performed where possible.

8 Calculation

The free dissolved concentration (C_W) of a contaminant in an equilibrated system can be calculated using:

$$C_W = \frac{N_R - Bl_R}{m_R \cdot K_{SW}}$$

In which N_R is the amount (ng) of compound measured in the extract of the sheet/bottle; Bl_R the procedural (solvent) blank (ng); m_R the mass of passive sampling material (kg) **after** exposure and K_{SW} the material-water partition coefficient (l/kg). The result obtained is in ng/l but it is often more conveniently expressed in pg/l.

9 Process QA

9.1 Depletion

To estimate the true free dissolved concentration (C_W) of contaminants that the sediment releases to the water phase at equilibrium requires that the amount depleted from the sediment to obtain the equilibrium should be minimal, as every reduction of the concentration in the sediment (C_S) will also result in a decrease in the concentration in the aqueous phase concentration. It should be noted that C_W is not necessarily proportional to the total concentration in the sediment. A 10% decrease in total sediment concentration could result in a 90% decrease in C_W, depending on the proportion of the target compound that is available for exchange with the water phase. The distribution of PRCs between the reference phase and the sediment phase indicates the capacity ratio of those two phases, provided that equilibrium was obtained. This distribution factor (DF) is the ratio of the amount of PRCs that remains on the PS and that sorbed by the sediment:

$$DF = \frac{N_R}{N_0 - N_R}$$

Where N_R is the amount measured on the reference phase after exposure and N_0 the amount spiked on the reference phase prior to exposure. When DF is 0.1 or less, the CW will not significantly be affected by depletion. Situations can occur in which this criterion for DF is met for PAHs but not for PCBs in the same sample. High DF values mean that there is little sorption capacity in the sediment and probably indicate that the sheet/bottle has depleted the sediment. The calculated C_W value will then be underestimated.

9.2 Equilibrium

The use of DF as estimation of depletion assumes that equilibrium has been attained. Depending on the conditions, this may not always be the case. For PCBs, it has been found that the capacity ratios between the reference phase and the sediment are rather equal for all congeners. Therefore similar values for DF are expected for PRCs with large difference in hydrophobicity, ie, that DF for PRCs such as CB010 and CB 204 do not differ a lot. It still has to be verified if this is the case for sediments over a large geographically range.

9.3 Environmental validation

Some validation of the method described here can be obtained from application of the method and comparison with parallel experiments using the same sediment in which sediment living organisms are equilibrated with the contaminated sediment. Concentrations in organism should be related to the C_W values obtained by passive sampling. So far, experiments have shown better agreement of internal concentration in organisms with PS results than with total concentrations in sediment. More data will be required for full validation.

10 References

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ANNEX A Coating of bottles

1. Bottles with small neck (max 4 cm) are engraved with a unique number.
2. Then washed thoroughly, dried at 100°C and weighed (0.001 g) without cap as an accidental exchange of caps would make the registered weight useless.
3. Weights are recorded in the bottle dictionary.
4. In a fume hood, a roller is prepared on which bottles can roll horizontally.
5. Teflon tubing (≥5mm ID) is fixed so it enters the bottle half way with one end, bended slightly downward, and the other end outside the bottle is bended upward and a small plastic funnel is connected to it. A thinner teflon tube (1-1.5 mm ID) is placed in parallel in the bottle and the other end connected to a nitrogen supply (3-5 l/min). This should all be fixed in such a way that the bottle can turn freely on the roller and bottles can be placed and removed without touching the tubing ends.
6. In a disposable glass jar or bottle of about 400 ml, 6 gram of silicone rubber paste is weighed.
7. Then 50 ml of pentane is added per gram of rubber paste.
8. The silicone rubber paste is dissolved by shaking and sonification (±15 min).
9. A bottle is placed on the roller with the tubing inside.
10. While rolling (3-6 rpm), the bottle is purged with N_2 for 1 minute and then the gas flow is stopped.
11. 25 ml pentane solution is added in the funnel with a disposable measuring cylinder.
12. The solution will spread over the walls of the bottle and the pentane will evaporate; this can be assisted with some N_2 flow.
13. When the pentane has evaporated, the bottle can be carefully taken away from the tubing, and rolled for another 5 minutes so the film does not sag away from the wall of the bottle.
14. Another bottle is placed around the tubing and coated in a similar way.
15. The films have to cure for at least three days at ambient temperature. If the humidity is lower than 50%, add a few drops of water to the bottle.
16. After curing (and drying) weights are recorded.
17. Then the coated bottles are twice pre-extracted overnight with 50 ml ethyl acetate to remove oligomers and contaminants.
18. The ethyl acetate is removed from the bottle. The bottles are placed upside-down on tissue-paper for 15 min and further dried horizontally (eventually assisted by N_2 flow) under the fume hood
19. After drying, weigh each bottle and record the weight in the bottle dictionary. Calculate the actual film weight for individual bottle number .

ANNEX B Candidates for Performance Reference Compounds (PRCs)

Performance Reference Compounds are required in order to measure the capacity ratio of the sampler and sediment. Characteristics of good candidates are PRCs, include:

- Stable in storage and during use of the sampler.
- Cover a wide range of Kow values matching that of the target analytes. Currently, a range of Kow of 3.5 – 7 is adequate.
- Not be found in the environmental matrices being sampled.
- Not interfere with the determination of target analytes, or of internal standards, recovery standards used in the determination of target analytes.
- Not be significantly toxic to the environment.
- Either be determined by the same method as the target analytes, or else be totally separable from them and determined by a different method.

	A better selection can be suggested after the evaluation of the PSTS data.
Deuterated PAHs	Using GCMS, nearly all deuterated PAH are applicable as PRC. A series of naphthalene, fluorene, phenanthrene, fluoranthene, chrysene, benz[*e*]pyrene and coronene is suitable for passive samplers in water as well as in sediment. If HPLC is used for PAH analysis, the choice of deuterated PRC is more limited. Coelution will easily give too high estimates of the residual PRC amounts on the film and consequently DF values will be overestimated. Deuterated fluoranthene, chrysene, perylene and coronene show lowest disturbance
PCBs	PCB 4, 10, 14, 21, 29, 30, 50, 55, 78, 104, 145, 155, 204 are all suitable congeners. The possibility of co-elution has not been sufficiently investigated for all compounds. This problem is also influenced by whether ECD or MS is used for detection.

ANNEX C Determination of Partition coefficients

Introduction

To calculate the concentration in the water phase (sediment pore water) from the analysis of passive samplers (or the concentrations in water if passive samplers are deployed in water), the partition coefficients (K_{SW}) of the sampler materials for the target contaminants are required. The determination of this parameter is not straightforward, as equilibrating a sampler with water as an undisturbed determination of the free dissolved concentration is not easily undertaken. A large volume of aqueous phase may be required, and the slightest amount of particulate matter may significantly disturb the concentration in the water phase.

A way to circumvent this difficulty is the use of the cosolvent method. In this approach, the K_{SW} is determined in mixtures of methanol-water in the range of 20 to 50% methanol. The measured $\log K_{SW}$ values of the reference phase are inversely related to the methanol content. By extrapolation to 0% methanol, the K_{SW} in 100% water can be determined. The much lower K_{SW} values in methanol-water mixtures means also lower sorption to particulate matter and bottle surfaces and can therefore be measured much more easily, and is mush less susceptible to confounding disturbances. In general, the target compounds are spiked onto the passive sampler material, and then the material is equilibrated with the various solvent mixtures. As a check for equilibrium, some of the deuterated analogues can be added to the aqueous phase.

Procedure

Preparations

Passive sampler material should first be pre-extracted as decribed above (e.g. through 100 hours soxhlet extraction with ethyl acetate). The sampler size can be at the same as used in exposures, but a smaller size can be used, and may be more convenient.

If the material of concern is to be used as a bottle coating, a sheet of this material can be obtained by coating a PE bottle. After sufficient curing, the bottle is cut into pieces of the required size and the coating material can then be peeled off for use.

Spiking and equilibration

The spiking with appropriate amount of test compounds (e.g. 500±50 ng for PAHs and 350±50 ng for PCBs) is performed as described for PRC compounds. If partition coefficients for deuterated compounds also need to be determined, these could be added subsequently. Alternatively they can be added to the aqueous phase instead.

Bottles of 2.5 to 1 litre volume with alufoil lined caps or glass stopper are filled up to 80% with methanol-water mixtures of 20, 25, 30, 35, 40, 45 to 50% methanol, prepared on weight basis. Milli-Q water (18.2 mΩ) is used. At this stage, the deuterated compounds can be added to the mixed methanol-water phase. Introduce a spiked sheet into each bottle, and a non-spiked sheet to a bottle containing 900 ml of 20 % methanol/water as procedural blank.

For partition coefficients in water only and 10% methanol/water mixture, sheets should be exposed in 10 L bottles. Extraction by separating funnel is quite laborious, and so it is suggested that a continuous batch extractor is used, which extracts the aqueous phase in a nearly closed system (Hermans *et al*., 1992).

The bottles are shaken on an orbital shaker at 125 rpm for 15 days, by which time equilibrium will have been attained.

Extraction and analyses

Two separating funnels (1 or 2 l) are rinsed with hexane and 100 ml hexane is added to each. After weighing the bottle, the methanol-water mixture or a portion that still allows proper shaking is poured into the first separating funnel. After extraction using 3 minutes of vigorous shaking followed by phase separation this portion is transferred to the second funnel, extracted again in similar way and subsequently discarded. Then the next portion is extracted until the complete volume has been extracted. Although sorption to the wall is considered negligible, the bottle is not further extracted as any sorbed compounds are not considered part of the aqueous phase and therefore will not contribute to the partitioning between the aqueous phase and the sampler material. The bottle is weighed again. For concentrations of methanol greater than 30%, smaller portions are transferred to the separating funnel and hexane extracted water is added to the funnel to reduce the methanol concentration to 30% or less. The hexane fractions are transferred to an evaporating flask by pouring it out of the top of the funnel, while carefully preventing any water from leaving the funnel. Funnels are washed with two times 25 ml of hexane which are added to the extract in the same way. Measuring internal standard is added and the extract is Kurdena-Danish (or equivalent apparatus) evaporated to the required volume for instrumental analysis, as described for exposed samplers.

The equilibrated samplers are taken from the bottle and extracted as described above for exposed sheets or bottles. Provided the pre-extraction was thorough, no cleanup is required. For the instrumental measurement only, addition of the measuring internal standard and Kurdena-Danish (or equivalent apparatus) concentration is required.

The reference phase-water partition coefficients (K_{SW}) are calculated by:

$$K_{SW} = \frac{C_R}{C_W}$$

The intercept of linear regression with the $\log(K_{SW})$ as y value and the mole fraction methanol as the x value will give the $\log(K_{SW})$ for 100% water.

Annex 10: Comments on the draft Technical Annex for the determination of PBDEs in marine sediments, prepared by a sub-group of WGMS 2007

Chapter 2
Concerning the sampling and the storage, polyethylene must not be used due to possible adsorption of the PBDE on this material. Moreover, all the glassware should be pre-baked before use (heat at 450°C overnight).

Chapter 4.1
The paragraph 4.1 concerning the "precautionary measures" should be placed at the beginning of the guideline. Indeed it presents general aspects useful for handling samples for PBDE analyses.

Chapter 4.3
Cellulose filter papers should not be used for the Accelerated Solvent Extraction. The glass fibre filters should be heated at 450°C overnight instead of 300°C for 24h.

Chapter 4.4:
For soxhlet extraction, other solvent mixture could be used like pentane/dichloromethane (DCM). For ASE, other solvent or mixture of solvents could also be used : DCM, toluene.

GPC clean-up is useful to remove fat in biota samples and may be not necessary when analyzing sediment.

For the clean-up step on column chromatography, the fractionation of the extract will depend on the sorbent and solvent used for elution: the PBDE will thus not always "elute in the second fraction".

When analysing sediment, the sulphur should be removed from the extract.

Chapter 4.5:
The drawbacks of the use of the Turbo-vap concentrator (losses and cross-contamination) should be more highlighted.

Toluene could also be used as solvent for injection.

Chapter 4.6:
The reference used for the $\log K_{ow}$ should be precised under the table 1.

Chapter 4.7:
Hydrogen could also be used as a carrier gas.
DB5-MS column could also be used as a non-polar column.
Lower LOD could be achieved with GC-LRMS-NCI : 0.005-0.05 µg kg^{-1} (BDE209: 0,01-0.12µg kg^{-1}).

Chapter 4.8.1:
CB112 is not suitable for recovery standards as it can be found in biota sample. BDE139 could used as a recovery standard.

Chapter 5.1:
PBDE standards are only commercially available in solution.

Chapter 5.2:
BDE 190 could also be used as internal standard

Chapter 5.3
BDE139 could also be used as recovery standard.

Chapter6:
Lower LOD could be achieved with GC-LRMS-NCI : 0.005-0.05 µg kg^{-1} (BDE209: 0,01-0.12µg kg^{-1}).
No certified reference material is available for sediments.

Annex 11: Technical Annex on the determination of PBDEs in sediment

Technical Annex — PBDEs in sediment

1. Introduction

This annex provides advice on polybrominated diphenyl ether (PBDE) analysis for sediment. The analysis of PBDEs in sediment generally involves extraction with organic solvents, clean-up and gas chromatographic separation with mass-spectrometric detection. All stages of the procedure are susceptible to insufficient recovery and/or contamination. Where possible, quality control procedures are recommended in order to check the method's performance. These guidelines are intended to encourage and assist analytical chemists to reconsider their methods and to improve their procedures and/or the associated quality control measures where necessary.

Polybrominated diphenyl ethers (PBDEs) constitute a group of additive flame retardants that are predominately found in electrical equipment, textiles and furniture. PBDEs are used as additives to polymers and resins and are thought to be more easily released to the environment compared to reactive flame retardants. PBDEs consist of two phenyl rings, connected by an ether bridge, each ring containing up to 5 bromine atoms. There are a possible 209 PBDE congeners depending on the position and number of bromines, with molecular weights ranging from 249 to 960 daltons. Congeners are named according to the International Union of Pure and Applied Chemistry (IUAPAC) numbering format developed for chlorobiphenyl (CB) congeners. However, PBDE technical mixtures used as flame retardants contain only a limited number of these congeners (~20). Commercial PBDE mixtures are classified according to the degree of bromination. The penta mix contains mainly tetra- to hexa-BDEs, the octa mix mainly hexa- to octa-BDEs and the deca mix containing mainly deca-BDE. Penta-BDE is primarily used in furniture and upholstery, octa-BDE in plastics, and deca-PBDEs in textiles and polymers. In the EU, a restriction on the use of the penta and octa technical mixture was put in place on 15 August 2004, restricting the use of the penta and the octa technical mixtures to a limit of 0.1% by mass for all articles placed in the market according to the European Directive 2003/11/EC[1], 24th amendment of 76/769/EEC.

PBDEs can be released to the environment during their production, while manufacturing other products, and during disposal of products containing these chemicals. In addition, PBDEs may continue to leak out of treated material and constitute a diffuse source of these compounds to the environment. Atmospheric transportation is a major pathway for PBDEs into the marine environment. Other possible pathways include direct discharge from point sources such as storm waters and waste water.

Due to the similarity in structure between PBDEs and CBs, PBDEs are expected to persist in the marine environment and exhibit similar toxic properties. PBDEs have high (Log $K_{ow} > 4$) octanol water partition coefficients ranging from 4.3 for di-BDE to 10.33 for deca-BDE (Table 1). PBDEs are hydrophobic and therefore tend to associate with particulate material and will accumulate in sediment particularly if it has a high organic carbon content.

2. Sampling and short-term storage

Plastic materials must not be used for sampling due to the possible absorption of PBDEs by the container material (Hard polyethylene (HPE), Polypropylene(PP) or polytetrafluorethene can only be applied for a short time period, few days, or when in frozen condition i.e. −20°C). Samples should be stored in solvent washed aluminium cans or glass jars. Aluminium cars are

better as glass jars are more susceptible to breakage. All glassware should be pre-baked before use (heat at 450°C overnight). Samples should be transported in closed containers; a temperature of 25°C should not be exceeded. If samples are not analysed within 48 h after sampling, they must be stored in the short term at 4°C. Storage over several months is only possible for frozen (<−20°C) and dried samples.

3. Pre-treatment and long term Storage

To increase comparability of data, samples can be wet sieved to reduce the variation of grain size distribution. This is particularly important for samples with less than 0.5 % organic carbon. PBDEs can be extracted from wet or dried samples, although storage, homogenisation and extraction are much easier when the samples are dry. Drying the samples however may alter the concentrations, e.g. by the loss of compounds through evaporation or by contamination. Losses and contamination during drying must be shown to be insignificant.

Chemical drying can be performed by grinding with Na_2SO_4 or $MgSO_4$ until the sample reaches a free-flowing consistency. It is essential that there are at least several hours between grinding and extraction to allow for complete dehydration of the sample; residual water will decrease the extraction efficiency. A parallel determination of dry weight should be performed to allow recalculation to dry weight. A further representative subsample should be used for determination of organic carbon to allow normalisation of data.

Freeze-drying is a popular technique, although its application should be carefully considered. Possible losses or contamination must be checked. Losses through evaporation are diminished by keeping the temperature in the evaporation chamber below 0°C. Contamination during freeze-drying is reduced by putting a lid, with a hole of about 3 mm in diameter, on the sample container.

Typically, the dry intake mass for PBDE analysis is between 10 and 100g, depending on the extraction method and the expected concentrations. Before taking a subsample for analysis, the samples should be sufficiently homogenised. Freeze dried samples can be stored at room temperature and wet sediment frozen, at −20°C or below.

More information is provided in the JAMP guidelines for monitoring contaminants in sediment

4 Analysis

4.1 Precautionary Measures

Special precautions are required in the laboratory when analysing PBDEs due to their sensitivity to UV light. PBDEs are prone to photolytic degradation; if exposed to UV light debromination can occur, especially for BDE209 (Covaci *et al.,* 2003; de Boer and Wells, 2006). Therefore, incoming light to the laboratory should be minimised by placing UV filters on the windows and over fluorescent lightings, or by not using any artificial lighting within the laboratory. It is recommended that all calibration and spiking standards are prepared and stored in amber glassware.

The use of plastics should be avoided as they can contain PBDEs. BDE209 can adsorb to dust particles and can be a source of contamination in the laboratory. Therefore, it is recommended that an ioniser be placed in the laboratory and the laboratory kept as dust free as possible. Heating of glassware in an oven (e.g. at 450°C overnight) can also be useful for removing PBDE contamination. In addition, all glassware should be covered with solvent-washed aluminium foil to keep out any dust. The degree of contamination, and its sources, will vary between laboratories. Blanks should be significantly lower than the concentrations found in field samples. In practice, analysts should adopt a methodical approach to

precautionary measures against contamination to determine the measures that are necessary in their particular circumstances to reduce blanks to acceptably low values, of acceptable variance.

4.2 Solvent Purity and Blanks

PBDEs, and especially BDE209, can stick to glassware (or any other materials with suitable sorption characteristics). This can result in contamination of glassware. For work at low concentrations, the use of high-purity solvents is essential, particularly when large solvent volumes are being used for column clean-up. All batches of solvents should be checked for purity by concentration of an aliquot of solvent by at least the same volume factor as used in the overall analytical procedure. Batches which show significant contamination, so as to interfere with analysis, should be rejected. All glassware should be solvent-rinsed immediately prior to use as it will collect contamination from the laboratory atmosphere during storage. Pre-cleaning of all reagents (alumina, silica, sodium sulphate, hydromatrix etc) is essential.

4.3 Preparation of materials

Solvents, reagents and adsorptive materials must be 'free' of PBDEs and other interfering compounds. If not, then they must be purified using appropriate methods. Reagents and absorptive materials should be purified by solvent extraction and/or by heating in a muffle oven as appropriate. Glass fibre materials (e.g. Soxhlet thimbles and filter papers used in Pressurised Liquid Extraction (PLE)) should be cleaned by solvent extraction or pre-baked at 450^{o}C overnight. It should be borne in mind that clean materials can be re-contaminated by exposure to laboratory air, particularly in urban locations, and so the method of storage after cleaning is of critical importance. Ideally, materials should be prepared immediately before use, but if they are to be stored, then the conditions should be considered critically. All containers which come into contact with the sample should be made of glass or aluminium, and should be pre-cleaned before use. Appropriate cleaning methods would include washing with detergents, rinsing with water of known quality, and finally solvent rinsing immediately before use. This method should also be used for the first step of cleaning of PLE cells which should be further washed through a complete cycle of extraction using the PLE. Heating of glassware in an oven (e.g. at 400°C for 24 hours) can also be useful for removing PBDE contamination.

4.4 Extraction and clean-up

The similarity in structure of the PBDEs to CBs means that techniques used for the analysis of CBs may also be applied to the analysis of PBDEs (de Boer *et al.*, 2001). PBDEs are hydrophobic and will have an affinity for particles and therefore can accumulate in sediment particularly if it has a high organic carbon content. A range of extraction methods have been used for the extraction of PBDEs from sediment. These include the more traditional methods such as Soxhlet and the newer automated methods such as Pressurised Liquid Extraction (PLE), Supercritical fluid extraction (SFE) has also been applied to PBDE extractions, although reproducibility was poor compared to Soxhlet (Covaci *et al.*, 2003). However, most laboratories are still using the traditional Soxhlet extraction. For soxhlets, hexane/acetone or other mixtures such as pentane/dichloromethane have been used for the extraction of PBDEs combined with an extraction time of between 6 and 24 h. Hexane/acetone mixtures are also used with PLE (if no fat retainers used) with an extraction time of ~ 10 min per sample. Other solvents such as dichloromethane or toluene may be used for PLE. PLE or soxhlet are therefore the preferred methods with PLE having the advantage of using less solvent, being fully automated and taking less time than Soxhlet. All glassware should be cleaned as indicated above, and septa replaced each time.

Sediment extracts will always contain many compounds other than PBDEs, and a suitable clean up is necessary to remove those compounds which may interfere with the subsequent analysis. Different techniques may be used, either singly or in combination, and the choice will be influenced by the selectivity and sensitivity of the final measurement technique and also by the extraction method employed. The most commonly used clean-up methods involve the use of alumina or silica adsorption chromatography, but gel permeation chromatography (GPC) is also employed, and is particularly effective at removing sulphur, which must be removed from the extract. Iso-hexane can be used elute alumina or silica columns. However, whatever method and solvent is used, the elution pattern of PBDEs should be determined and carefully checked, particularly for BDE209. When applying gel permeation chromatography (GPC), two serial columns are sometimes used to remove potentially interfering substances. Solvent mixtures such as dichloromethane/hexane or cyclohexane/ethyl acetate can be used as eluents for GPC. However, a second clean-up step is often required to separate the PBDEs from other organohalogenated compounds. One advantage of GPC is that it can also be used to remove sulphur from the extracts. When silica columns are used, the PBDEs will elute in the second, more polar, fraction (along with the organochlorine pesticides). However, this will be dependent on the solvents used and the adsorbents and the degree of deactivation. PBDEs are stable under acid conditions; therefore treatment with sulphuric acid or acid impregnated silica columns may be used in the clean-up.

One advantage of using PLE extraction is that it is possible to combine the clean up with the extraction, especially where mass spectrometry will be used as the detection method. Methods have been developed by Lund University for online clean-up and fractionation of dioxins, furans and PCBs with PLE for food, feed and environmental samples (Sporring *et al.*, 2003). The first method utilises a fat retainer for the on-line clean-up of fat. Silica impregnated with sulphuric acid, alumina and florisil have all been used as fat retainers. A non-polar extraction solvent such as hexane should be used if fat retainers are used during PLE. This method can also be applied to the extraction of PBDEs in sediment as well as biota. However, problems have been highlighted with BDE209 which can be lost during PLE extraction through adsorption on to the extraction system tubing. However, with careful optimisation it is possible to use PLE for BDE209. Losses of BDE209 may be accounted for by using labeled ^{13}C BDE209 as an internal standard.

For GC/MS analysis, sulphur should be removed from the extracts in order to protect the detector. This can be achieved by the addition of copper powder, wire or gauze during or after Soxhlet extraction. Ultrasonic treatment might improve the removal of sulphur. As an alternative to copper, other methods can be used (Smedes and de Boer, 1997).

4.5 Pre-concentration

Samples can safely be concentrated using a Kuderna Danish system. Alternatively more modern Turbo-vap sample concentrators can be used to reduce solvent volume. This is a rapid technique, but needs to be carefully optimised and monitored to prevent both losses (both of volatiles and solvent aerosols) and cross-contamination. The use of rotary-film evaporators is more time consuming but more controllable. However, evaporation of solvents using this technique should be performed at low temperature (water bath temperature of $\leq 30°C$) and under controlled pressure conditions, in order to prevent losses of the more volatile PBDEs. For the same reasons, evaporation to dryness should be avoided at all costs. Syncore systems are also more controllable but as rapid as Turbo-vaps and have the advantage of automatically rinsing down the sides of the vial (if the flushback module fitted) while concentrating. Again water-bath temperatures should be minimised to prevent losses. When reducing the sample to the required final volume, solvents can be removed by a stream of clean nitrogen gas. Suitable solvents for injection into the gas chromatograph (GC) include hexane, heptane, toluene and *iso*-octane.

4.6 Selection of PBDEs to be determined

PBDE technical mixtures used as flame retardants contain only a limited number of the possible 209 congeners (~20). The penta mix contains mainly tetra- to hexa-BDEs, the octa mix mainly hexa- to octa-BDEs and the deca mix containing mainly deca-BDE. Nine BDE congeners have been detected in the penta mix, the major ones being BDE47 (37%) and BDE99 (35%). The octa mix contains hexa- to octa-brominated congeners, with the main congener being BDE183, a hepta-brominated congener. The deca mix contains 98% decaBDE (BDE209).

Concentrations of PBDE congeners currently analysed vary considerably, however the congener pattern found in environmental samples is relatively consistent. Most laboratories analyse for the penta-mix compounds, tetra- to hexa-BDEs. In addition, these congeners are thought to be the most toxic and likely to bioaccumulate. In sediment BDE28, 47, 85, 99, 100, 153, 154 are normally found. BDE183 is occasionally found but as a representative of the octa-mix should also be included in any congener list. Other BDE congeners also measured and occasionally found include BDE66 and 85, a tetra- and penta-BDE, respectively. BDE 209 is less frequently measured, due to the analytical difficulties, but when it is it can often be the dominant congener in sediment. Law *et al*. (2006) proposed a minimum congener set for use when determining BDEs to cover all three technical mixtures and what is commonly found in biota and sediment. This list consisted of BDE28, BDE47, BDE99, BDE100, BDE153, BDE154, BDE183 and BDE209. This list is consistent with the congeners required by the QUASIMEME Scheme for both biota and sediment and are routinely measured by the majority of laboratories. However, it is apparent that other congeners are found in marine samples (e.g. BDE 66 and 85) and so should also be analysed.

Standards are available for all these congeners. Table 1 lists the PBDEs most commonly monitored

Table 1. Congeners commonly monitored in environmental samples along with their degree of bromination, chemical name and the octanol water partition coefficient (Log K_{OW}), where available (Braekevelt *et al., 2003*).

PBDE Congener	Number of Br	Name	Log K_{OW}
BDE17	3	2,2',4-tribromodiphenyl ether	5.74
BDE28*	3	2, 4,4'-tribromodiphenyl ether	5.94
BDE75	4	2, 4,4', 6-tetrabromodiphenyl ether	
BDE49	4	2, 3,4, 5'-tetrabromodiphenyl ether	
BDE71	4	2, 3', 4', 6-tetrabromodiphenyl ether	
BDE47*	4	2, 2',4, 4'-tetrabromodiphenyl ether	6.81
BDE66	4	2, 3',4, 4'-tetrabromodiphenyl ether	
BDE77	4	3, 3',4, 4'-tetrabromodiphenyl ether	
BDE100*	5	2, 2',4, 4', 6-pentabromodiphenyl ether	7.24
BDE119	5	2, 3',4, 4', 6-pentabromodiphenyl ether	
BDE99*	5	2, 2',4, 4', 5-pentabromodiphenyl ether	7.32
BDE85	5	2, 2',3, 4, 4'-pentabromodiphenyl ether	7.37
BDE154*	6	2, 2',4, 4', 5, 6'-hexabromodiphenyl ether	7.82
BDE153*	6	2, 2',4, 4', 5, 5'-hexabromodiphenyl ether	7.90
BDE138	6	2, 2',3, 4, 4', 5'-hexabromodiphenyl ether	
BDE190	7	2,3,3',4,4',5,6-heptabromodiphenyl ether	
BDE183*	7	2,2',3,4,4',5',6-heptabromodipheny l ether	8.27
BDE209*	10	Decabromodiphenyl ether	10.33

*** Congeners proposed by Law *et al.* as a minimum congener set for use when determining BDEs; they are also included in the QUASIMEME scheme**

4.7 Instrumental determination of PBDEs

Splitless, pulsed-splitless, programmed temperature vaporiser (PTV) and on-column injectors have been used for the determination of PBDEs, all of which are capable of yielding good results if optimised. Automatic sample injection should be used wherever possible to improve the reproducibility of injection and the precision of the overall method. For PBDE analysis, the cleanliness of the liner is very important if adsorption effects and discrimination are to be avoided, and the analytical column should not contain active sites to which PBDEs, particularly BDE209, can be adsorbed. Helium is the preferred carrier gas, and only capillary columns should be used. Mainly non-polar columns are used, e.g. HT-8, DB1701, DB5 and STX-500 (DB1 is usually used for BDE209) Korytar *et al.* (2005) provide comprehensive information on various capillary columns used for PBDE analysis. Baseline separation should be achievable for all BDEs listed in Table 1. However, BDE31 may coelute with BDE28. Because of the wide boiling range of the PBDEs to be determined and the surface-active properties of the higher PBDEs, the preferred column length is 25–50 m, with an internal diameter of 0.1 mm to 0.3 mm. Film thicknesses around 0.2 µm are generally used.

BDE209 can be measured in the same run but will give a smaller and broader peak compared to other PBDEs. Detection limits will be approximately 10 fold higher for BDE209. Since the retention time is long, the determination of BDE209 is often done separately using thinner films (0.1 µm) and/or a shorter column, both of which have been found to improve the detection of BDE209.

4.8 Detection Methods

4.8.1 General

Either gas chromatography- mass spectrometry (GC-MS) or GC- MS-MS (ion trap or triple quadropole) should be used. Both high and low resolution GC-MS can be used in conjunction with either electron ionisation (EI) or electron capture negative ionisation (ECNI). Although gas chromatography-high resolution mass spectrometry with electron impact ionisation (GC-HRMS) is the best method to unambiguously identify and quantify PBDEs in environmental samples, the expense and limited availability means that most laboratories use low resolution GC-MS normally in ECNI mode. Lower brominated PBDEs (mono- and di-BDEs) show better sensitivity in EI mode. However, the higher brominated PBDEs (> 3 bromines) give better sensitivity using the ECNI mode; limits of detection for these congeners are approximately 10 fold lower in ECNI compared to EI. ECNI shows improved sensitivity compared to positive impact chemical ionisation (PCI). Therefore, GC-ECNIMS is used most frequently for the analysis of PBDEs in environmental samples. Either ammonia or methane may be used as the reagent gas when using chemical ionisation.

4.8.1 GC-MS

The base ions detected using ECNI are the bromine ions (*m/z* = 79/81) for the tri- to hepta-BDEs. BDE congeners show the typical ^{79}Br (50.5%) and ^{81}Br (49.5%) isotope distribution pattern. One of the drawbacks of the CI mode is that isotopically labelled standards (^{13}C) cannot be used as internal standards for quantification purposes when only the bromide ions are monitored. However, mono fluorinated BDEs may be used as internal standards. Alternatively using GC-ECNI-MS a recovery standard can be added prior to extraction. CB198 and other halogenated compounds not present in environmental samples can be used as recovery standards. Larger fragment ions, necessary for confirmation, are only found for BDE209. These are formed by the cleavage of the ether bond to give the pentabromo phenoxy ion (*m/z* = 484/486). In general an internal standard method should be used for the quantification of PBDEs.

One advantage of using EI is that ^{13}C labelled internal standards may be used. The major ions formed in EI mode are the molecular ions which can be used for identification and quantification purposes. Other fragment ions are also formed in EI mode which can be used as confirmatory ions.

4.8.2 Possible pitfalls and solutions

Degradation of PBDEs, particularly BDE209, can occur on the GC. The presence of a hump or rising baseline before BDE209 is an indication of degradation during injection, whereas the presence of lower brominated BDE (nona-, octa- and eventually other lower brominated BDEs) indicates possible degradation during extraction and clean-up. To minimise this, the GC liners and injection syringe should be changed regularly. Silanising both the syringe and liner may help. When using on-column injection, the choice of retention gap can also have an effect on the degradation of BDE209 during analysis. Deactivated fused silica retention gaps are often used. The QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring) external quality assurance scheme has also highlighted the difficulties with the analysis of BDE209 with CV% for this congener ranging from 40 – 256%. As a result, many laboratories do not analyse for BDE209.

5. Calibration and Quantification

5.1 Standards

Standard solutions of known purity should be used for the preparation of calibration standards. Contaminants in the standard must not interfere with determination of any of the target analytes. If the quality of the standard materials is not guaranteed by the producer or supplier (as for certified reference materials), then it should be checked by GC-MS analysis. Solid standards should be weighed to a precision of 0.1–0.5%. In addition, certified standard solutions are available from QUASIMEME and other suppliers for cross-checking. Calibration standards should be stored in the dark because some PBDEs are photosensitive, and ideally solutions to be stored should be sealed in amber, glass ampoules. Otherwise, they can be stored in a refrigerator in stoppered measuring cylinders or flasks that are gas tight to avoid evaporation of the solvent during storage.

Ideally, internal standards should fall within the range of the compounds to be determined, and should not include compounds which may be present in the samples. A range of ^{13}C-labelled PBDEs are available for use as internal standards in PBDE analysis using GC-EIMS. However, when using GC-ECNIMS these are of little value as, for the majority of congeners, only the bromine ions can be monitored. For BDE209 a high molecular weight fragment is formed during GC-ECNIMS and, therefore, ^{13}C labelled BDE209 should be used. When GC-ECNIMS is used mono fluorinated BDEs may be used as internal standards or a recovery standard added to each sample prior to extraction and the recovery calculated as a check on the method.

5.2 Calibration

Multilevel calibration with at least five calibration levels is preferred to adequately define the calibration curve. In general, GC-MS calibration is linear over a considerable concentration range but exhibits non-linear behaviour when the mass of a compound injected is low due to adsorption. The use of a syringe standard is recommended, for example BDE190. Quantification should be conducted in the linear region of the calibration curve, or the non-linear region must be well characterised during the calibration procedure. Internal standardisation should be used for the quantification of PBDEs. Linearity of response in samples may be controlled using further internal standards at different concentrations, or a standard addition technique can be used.

6. Analytical Quality Control

Planners of monitoring programmes must decide on the accuracy, precision, repeatability, and limits of detection and determination which they consider acceptable. Minimum achievable limits of determination for each individual component should be as follows:

- for GC-ECNIMS measurements: 0.05 μg kg^{-1} dry weight for tri- to hepta-BDE and 0.50 μg kg^{-1} dry weight for BDE209; Often lower LOD could be achieved : 0.005 to 0.05 μg kg^{-1} dry weight (BDE209 0.01 to 0.12 μg kg^{-1};
- for GC-EIMS: 0.5 μg kg^{-1} dry weight.

A procedural blank should be measured with each batch of samples, and should be prepared simultaneously using the same chemical reagents and solvents as for the samples. Its purpose is to indicate sample contamination by interfering compounds, which will result in errors in quantification. Recoveries should be checked for all samples using selected recovery internal standards. A second confirmation of recovery may be obtained by passing a standard through the whole analytical procedure Recoveries should be between 70 and 120%; if not analyses should be repeated. The procedural blank is also very important in the calculation of limits of detection and limits of quantification for the analytical method. In addition, a laboratory reference material (LRM) should be analysed within each sample batch. No certified reference materials are available for sediment. The LRM must be homogeneous and well-characterised for the determinands of interest within the analytical laboratory. Ideally the LRM determinand concentrations should be in the same range as those in the samples. The data produced for the LRM in successive sample batches should be used to prepare control charts. It is also useful to analyse the LRM in duplicate from time to time to check within-batch analytical variability. The analysis of an LRM is primarily intended as a check that the analytical method is under control and yields acceptable precision. At regular intervals, the laboratory should participate in an intercomparison or proficiency exercise in which samples are circulated without knowledge of the determinand concentrations, in order to provide an independent check on performance.

7. Data Reporting

The calculation of results and the reporting of data can represent major sources of error. Control procedures should be established in order to ensure that data are correct and to obviate transcription errors. Data stored on databases should be checked and validated, and checks are also necessary when data are transferred between databases. If possible data should be reported in accordance with the latest ICES reporting formats.

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Annex 12: Technical Annex on the determination of HBCD in sediment

Technical Annex — Hexabromocyclododecane (HBCD) in sediment

1. Introduction

This annex provides advice on hexabromocyclododecane (HBCD) analysis for sediment. The analysis of HBCD in sediment generally involves extraction with organic solvents, clean-up and either gas chromatographic separation with mass-spectrometric (MS) detection or liquid chromatography with MS detection. All stages of the procedure are susceptible to insufficient recovery and/or contamination. Where possible, quality control procedures are recommended in order to check the method's performance. These guidelines are intended to encourage and assist analytical chemists to reconsider their methods and to improve their procedures and/or the associated quality control measures where necessary.

HBCD is produced by the bromination of cycldodec-1,5,9-triene and has been used since the late 1970s. HBCD is an additive flame retardant that is predominately used in foams and expanded polystyrene and in textile back coatings. HBCD can be released to the environment during its production and while manufacturing other products, and during disposal of products containing this chemical. In addition, HBCD may continue to leak out of treated material and constitute a diffuse source of this compound to the environment. Atmospheric transportation is thought to be a major pathway for HBCD into the marine environment; HBCD has been found in remote areas of Sweden and Finland and in the Arctic.

Theoretically, there are sixteen possible stereoisomers of HBCD; 6 enantiomeric pairs and 4 meso forms. However, in technical HBCD mixtures mainly three of the 6 enatiomeric pairs are found, namely α-, β- and γ-HBCD, with the dominant isomer being γ-HBCD (Law *et al.*, 2005). In sediment the γ- isomer also dominates but in biota the major isomer is α-HBCD. β-HBCD is always a minor component. HBCD has a high octanol water partition coefficient (Log K_{ow} = 5.8). HBCD is hydrophobic and therefore will tend to associate with particulate material and will accumulate in sediment particularly if it has a high organic carbon content.

2. Sampling and short-term storage

Sample contamination may occur during sampling, sample handling, pre-treatment and analysis, due to the environment, the containers or packing materials used, the instruments used during sample preparation, and from the solvents and reagents used during the analytical procedures. Controlled conditions are therefore required for all procedures on-board ship. It is important that the likely sources of contamination are identified and steps taken to preclude sample handling in areas where contamination can occur. A ship is a working vessel and there can always be procedures occurring as a result of the day-to-day operations (deck cleaning, automatic overboard bilge discharges, etc.) which could affect the sampling process. One way of minimising the risk is to conduct any sample manipulation in a clean area, such as within a laminar-flow hood, away from the deck areas of the vessel. Plastic materials must not be used for sampling due to the possible absorption of contaminants by the container material (if not avoidable hard polyethylene (HPE), Polypropylene(PP) or polytetrafluorethene can only be applied for a short time period, few days, or when in frozen condition, i.e. −20°C). Samples should be stored in solvent washed aluminium cans or glass jars. Aluminium cans are better as glass jars are more susceptible to breakage. Samples should be transported in closed containers; a temperature of 25°C should not be exceeded. If samples are not analysed within

48 h after sampling, they must be stored in the short term at 4°C. Storage over several months is only possible for frozen (<-20°C) and dried samples.

3. Pre-treatment and long term Storage

To increase comparability of data, samples can be wet sieved to reduce the variation of grain size distribution. This is particularly important for samples with less than 0.5 % organic carbon. HBCD can be extracted from wet or dried samples, although storage, homogenisation and extraction are much easier when the samples are dry. Drying the samples however may alter the concentrations *e.g.* by the loss of compounds through evaporation or by contamination. Losses and contamination during drying must be shown to be insignificant. Chemical drying can be performed by grinding with Na_2SO_4 or $MgSO_4$ until the sample reaches a free-flowing consistency. It is essential that there are at least several hours between grinding and extraction to allow for complete dehydration of the sample; residual water will decrease extraction efficiency. A parallel determination of dry weight should be performed to allow recalculation of analytical results to a dry weight basis. A further representative subsample should be used for determination of organic carbon to allow normalisation of data

Freeze-drying is a popular technique, although its application should be carefully considered. Possible losses or contamination must be checked. Losses through evaporation are diminished by keeping the temperature in the evaporation chamber below 0°C. Contamination during freeze-drying is reduced by putting a lid, with a hole of about 3 mm in diameter, on the sample container.

Before taking a subsample for analysis, the samples should be sufficiently homogenised. Freeze dried samples should be stored at room temperature and wet sediment frozen, at -20°C or below.

More information is provided in the JAMP guidelines for monitoring contaminants in sediment.

4 Analysis

4.1 Solvent Purity and Blanks

For work at low concentrations, the use of high-purity solvents is essential and particularly when large solvent volumes are being used for extraction and column clean-up. All batches of solvents should be checked for purity by concentration of an aliquot of solvent by at least the same volume factor as used in the overall analytical procedure. Batches which show significant contamination, which will interfere with analysis, should be rejected. All glassware should be solvent-rinsed immediately prior to use as it will collect contamination from the laboratory atmosphere during storage. Heating of glassware in an oven (e.g. at 450°C for 24 hours) can also be useful in removing contamination. Pre-cleaning of all reagents (alumina, silica, sodium sulphate, hydromatrix, etc.) is essential.

4.2 Preparation of materials

Solvents, reagents and adsorptive materials must be free of HBCD and other interfering compounds. If not, then they must be purified using appropriate methods. Reagents and absorptive materials should be purified by solvent extraction and/or by heating in a muffle oven as appropriate. Glass fibre materials (e.g. Soxhlet thimbles and filter papers used in pressurised liquid extraction (PLE)) should be cleaned by solvent extraction or pre-baked at 450^{o}C overnight. It should be borne in mind that clean materials can be re-contaminated by exposure to laboratory air, particularly in urban locations, and so storage after cleaning is of

critical importance. Ideally, materials should be prepared immediately before use, but if they are to be stored, then the conditions should be considered critically. All containers which come into contact with the sample should be made of glass or aluminium, and should be pre-cleaned before use. Appropriate cleaning methods would include washing with detergents, rinsing with water and finally solvent rinsing immediately before use. This method should also be used for the first step of cleaning of PLE cells which should be further washed through a complete cycle of extraction using the PLE.

4.3 Extraction and clean-up

HBCD is hydrophobic and will have an affinity for particles and therefore can accumulate in sediment particularly if it has a high organic carbon content. HBCD can be extracted using extraction techniques used for other lipophilic, non-polar compounds such as CBs and PBDEs (Morris *et al.*, 2006). A range of extraction methods have been used for the extraction of HBCD from sediment. These include the more traditional methods such as Soxhlet or Ultra Turrax homogenisation and newer automated methods such as pressurised liquid extraction (PLE). However, most laboratories are still using the traditional Soxhlet extraction. For Soxhlets, hexane/acetone mixtures are commonly used combined with an extraction time of between 6 and 24 hrs. Hexane/acetone mixtures are also used with PLE (if no fat retainers used) with an extraction time of ~ 10 min per sample. PLE or Soxhlet are therefore the preferred methods with PLE having the advantage of using less solvent, being fully automated and taking less time than Soxhlet.

Sediment extracts will always contain many compounds other than HBCD, and a suitable clean up is necessary to remove those compounds which may interfere with the subsequent analysis. Different techniques may be used, either singly or in combination, and the choice will be influenced by the selectivity and sensitivity of the final measurement technique and also by the extraction method employed. The most commonly used clean-up methods involve the use of alumina or silica adsorption chromatography, but gel permeation chromatography (GPC) can also be employed. For GPC, two serial columns are often used. Solvent mixtures such as dichloromethane/hexane or cyclohexane/ethyl acetate can be used as eluents for GPC. Depending on the detection method being used it may be necessary to use a second clean-up step to separate HBCD from other orgnaohalogenated compounds. This is especially critical when using electron capture detection (ECD). HBCD is stable under acid conditions; therefore treatment with sulphuric acid or acid impregnated silica columns may be used in the clean-up.

One advantage of using pressurised liquid extraction (PLE) is that it is possible to combine the clean up with the extraction, especially where mass spectrometry is being used as the detection method. Methods have been developed by Lund University for online clean-up and fractionation of dioxins, furans and PCBs with PLE for food, feed and environmental samples (Sporring *et al.* 2003). The first method utilises a fat retainer for the on-line clean-up of fat. Silica impregnated with sulphuric acid, alumina and florisil have all been used as fat retainers. A non-polar extraction solvent such as hexane should be used if fat retainers are used during PLE. This method can also be applied to the extraction of HBCD in sediment as well as biota. However, if tetrabromobisphenol A (TBBP-A) is also to be extracted, this method is not possible due to retention on the fat retainer.

For GC/MS analysis, sulphur should be removed from the extracts in order to protect the detector. This can be achieved by the addition of copper powder, wire or gauze during or after Soxhlet extraction. Ultrasonic treatment might improve the removal of sulphur. As an alternative to copper, other methods can be used (Smedes and de Boer, 1997).

4.4 Pre-concentration

Turbo-vap sample concentrators can be used to reduce solvent volume. The use of rotary-film evaporators is more time consuming but more controllable. Buchi Syncore systems are also more controllable and are as rapid as Turbo-vaps and have the advantage of automatically rinsing down the sides of the vial (if flushback module fitted) while concentrating. In contrast to PBDEs and CBs where the evaporation steps have to be carefully optimised to avoid losses of the lower brominated/chlorinated compounds, loss of HBCD during concentrations is not an issue. When reducing the sample to final a volume, solvents can be removed by a stream of clean nitrogen gas. Suitable solvents for injection into the gas chromatograph (GC) include pentane, hexane, heptane and *iso*-octane. For analysis by LC-MS samples are normally taken to dryness and reconstituted in methanol.

4.5 Instrumental determination of HBCD

Analysis of HBCD is less straightforward than the analyses of PBDEs and a different approach is normally required. HBCD can be determined by gas chromatography- mass spectrometry (GC-MS), but the analysis can be problematic. The uncertainty is greater than for PBDEs analysed using the same method (Covaci *et al.*, 2003). In addition, the three main HBCD diastereoisomers found in technical mixtures cannot be separated by GC and a total concentration only can be determined. A liquid chromatography (LC) method is required to separate the three diastereoisomers, with separation of enantiomers being possible with a chiral HPLC column.

4.5.1 GC-MS

Few publications analyse HBCD along with the PBDEs by GC-MS, although it has been done using both GC-electron capture negative ionisation (ECNI) and high resolution GC-MS. GC-electron capture detection (ECD) is rarely used due to the limited linear range, and lack of selectivity. If GC-ECD is used then the clean-up will need to separate out all other organohalogenated compounds which may give co-elution problems. Splitless, pulsed-splitless, programmed temperature vaporiser (PTV) and on-column injectors have been used for the determination of HBCD. Automatic sample injection should be used wherever possible to improve the reproducibility of injection and the precision of the overall method. Mainly non-polar columns are used with the most commonly used columns being HT-8, DB1701, STX-500 and DB1. Both high and low resolution GC-MS can be used in conjunction with either electron ionisation (EI) or ENCI. Most laboratories using GC for HBCD use low resolution GC-MS normally in ENCI mode. ENCI shows improved sensitivity compared to EI or positive impact chemical ionisation (PCI). When GC-ENCIMS is used, the bromide ion is monitored. One of the drawbacks of the CI mode is that isotopically labelled standards (^{13}C) cannot be used as internal standards for quantification purposes when only the bromide ions are monitored. Larger fragment ions, required for structural confirmation are not formed in ENCI mode. Either ammonia or methane may be used as the reagent gas when using chemical ionisation.

HBCD isomers interconvert at temperatures >160^{o}C, therefore the three HBCD diastereoisomers cannot be separated and a broad hump is obtained in the GC chromatogram. In addition, the three diastereoisomers will have different response factors and, therefore, the concentration of HBCD cannot be determined accurately by GC-MS (Wells and de Boer, 2006). Furthermore HBCD degrades at 240^{o}C, therefore, there may be significant losses of HBCD during GC analysis. Cold on-column injection, short GC columns and thin stationary films can minimise the degradation of HBCD. When analysing for HBCD by GC-MS, the

liner should be changed after each batch of samples to keep it as clean as possible. Co-elution of HBCD with certain PBDEs can also be a problem.

4.5.2 LC-MS

A reverse phase column should be used for analysis of HBCD by LC-MS. The three diastereoisomers found in the technical mixture should separate easily using a column such as a C_{18} and either methanol/water or acetonitrile/water, normally buffered with ammonium acetate (10 mM), as the mobile phase. Typically the flow rate will be around 250 µl min^{-1} and a gradient programme will be required. HPLC with chiral columns such as permethylated β-cyclodextrin columns can also be used to separate the enantiomers of the α, β, γ-HBCD diastereoisomers. Either electrospray or atmospheric pressure chemical ionisation (APCI) can be used. However, electrospray is more sensitive and is therefore recommended. Clean-up of the samples before analysis is important to avoid matrix effects and ion suppression. The deprotonated molecular ion (m/z = 640.7) should be the major ion, fragment ions may also be identified to be used as qualifier ions. LC-MS has been reported to have poorer detection limits compared to GC-MS, with the sensitivity being approximately 10 times less than that of the GC-ENCIMS method. Using LC-MS and with an injection volume of ~15 µl, it should be possible to detect around 0.5 ng on column (Morris *et al.*, 2004).

5. Calibration and Quantification

5.1 Standards

Crystalline HBCD standard solutions for each of the three major stereoisomers (α-, β- and γ-HBCD) of known purity should be used for the preparation of calibration standards. If the quality of the standard materials is not guaranteed by the producer or supplier (as for certified reference materials), then it should be checked by GC-MS analysis. In addition, certified standard solutions are available from QUASIMEME and other suppliers for cross-checking. Calibration standards should be stored in the dark, and ideally solutions to be stored should be stored in sealed amber glass ampoules. Otherwise, they can be stored in a refrigerator in stoppered measuring cylinders or flasks that are gas tight to avoid evaporation of the solvent during storage.

Ideally, internal standards should fall within the range of the compounds to be determined, and should not include compounds which may be present in the samples. Deuterated and ^{13}C-labelled HBCD standards are available for the three major diastereoisomers for use as internal standards in HBCD analysis using GC-EIMS or LC-MS. However, deuterated standards are less expensive and are therefore the preferred option. As HBCD is prone to ion suppression it is recommended that a labelled standard should be used for each isomer being analysed by LC-MS. When using GC-ENCIMS these are of little value as only the bromine ions can be monitored. When GC-ENCIMS is used for the analysis a recovery standard should be added to each sample prior to extraction and the recovery calculated as a check on the method.

5.2 Calibration

Multilevel calibration with at least five calibration levels is preferred to adequately define the calibration curve. In general, GC-MS or LC-MS calibration is linear over a considerable concentration range but exhibits non-linear behaviour when the mass of a compound injected is low due to adsorption. Quantification should be conducted in the linear region of the calibration curve, or the non-linear region must be well characterised during the calibration procedure. External standardisation is used for HBCD with GC-ENCIMS as the bromine ions

only are monitored. An internal standard method may be used when GC-EIMS or LC-MS is used.

6. Analytical Quality Control

Planners of monitoring programmes must decide on the accuracy, precision, repeatability, and limits of detection and determination which they consider acceptable. Achievable limits of determination for each individual component are as follows:

- for GC-ENCIMS: 0.05 μg kg^{-1} wet weight
- for LC-MS: 0.5 μg kg^{-1} wet weight.
- for LC-MS/MS: 0.05μg kg^{-1} wet weight

A procedural blank should be measured with each batch of samples, and should be prepared simultaneously using the same chemical reagents and solvents as for the samples. Its purpose is to indicate sample contamination by interfering compounds, which will result in errors in quantification. The procedural blank is also very important in the calculation of limits of detection and limits of quantification for the analytical method. For GC-EIMS or LC-MS analysis, labelled standards can be added after or prior to extraction, whilst those from which the absolute recovery will be assessed are added prior to GC-MS injection. This ensures that the calculated HBCD concentrations are corrected for the recovery obtained in each case. For GC-ECNI-MS, recovery of HBCD should be checked and reported. In the case of GC-ECNI-MS a recovery standard such as CB198 should be added prior to extraction and the recovery calculated for each sample, by reference to an external standard.

In addition, a laboratory reference material (LRM) or certified reference material (CRM) should be analysed within each sample batch if available. The LRM must be homogeneous and well-characterised for the determinands of interest within the analytical laboratory. Ideally the LRM or CRM should be of the same matrix type (e.g., liver, muscle, mussel tissue) as the samples, and the determinand concentrations should be in the same range as those in the samples. The data produced for the LRM or CRM in successive sample batches should be used to prepare control charts. It is also useful to analyse the LRM or CRM in duplicate from time to time to check within-batch analytical variability. The analysis of an LRM is primarily intended as a check that the analytical method is under control and yields acceptable precision. A CRM may be analysed periodically in order to check the method bias. The availability of biota CRMs certified for HBCD is very limited. At regular intervals, the laboratory should participate in an intercomparison or proficiency exercise in which samples are circulated without knowledge of the determinand concentrations, in order to provide an independent check on performance.

7. Data Reporting

The calculation of results and the reporting of data can represent major sources of error. Control procedures should be established in order to ensure that data are correct and to obviate transcription errors. Data stored on databases should be checked and validated, and checks are also necessary when data are transferred between databases. If possible data should be reported in accordance with the latest ICES reporting formats.

8. References

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Sporring, S., Wiberg, K., Bjorklund, E., and Haglund, P. 2003. Combined extraction/Clean-up strategies for fast determination of PCDD/Fs and WHO PCBs in food and feed samples using accelerated solvent extraction, Organohalogen Compounds, 60–65, Dioxin 2003, Boston.

Annex 13: Comments on the draft Technical Annex for the determination of Alkylated PAHs in marine sediments, prepared by a sub-group of WGMS 2007

Chapter 2
Concerning the sampling and the storage, polyethylene must not be used due to possible adsorption of the PAHs on this material. Moreover, the use of glass or aluminium containers should be recommended.

Chapter 3:
The glassware and the glass fiber filters used for ASE can be pre-baked at 450°C overnight.

Chapter 5.3
The drawbacks of the use of the Turbo-vap concentrator (losses and cross-contamination) should be more highlighted.
The description of the drawbacks of the rotary evaporator should be reworded.

Chapter 5.4:
title???

Chapter 6/ chapter 9:
LOD should be expressed in dry weight of sediment.

The alkylated compounds are numerous individual substituted PAHs. Many of these compounds are not completely resolved by conventional gas chromatographic separations. Therefore, the method of quantification of these compounds for joint international monitoring programs should be precisely defined in order to assure comparability between the results. The alkyl homologues may be quantified in different ways:

- as summed concentrations of identified peaks (method 1);
- as summed concentrations of identified window of the retention times (method 2);
- as selected identified compounds.

Annex 14: Expert knowledge and guidance to ICES Data Centre

.METEX 2.2 codes reported together with metal analyses (more codes exist). The 3th column gives an indication if the digestion would be considered Total (Tot), partial strong (Ps), Partial weak (Pw), extraction not intended to be complete (Pe) and not relevant (nr). The last column shows the number of HM data reported using that method

ID nr	Metex	Digestion	1
	HFB0		240
1	ALKF	Tot	
2	AQR	Pw	338
3	AQR1	Pw	
4	AQRM	Pw	13
5	AQRX	Pw	48
6	EXO	nr	
7	EXOD	nr	
8	HAC0	Pe	
9	HCL	nr	
10	HCLA	nr	
11	HFB	Tot	3732
12	HFB1	Tot	4395
13	HFB2	Tot	
14	HFBM	Tot	56
15	HFBz	Tot	1285
16	HFC	Tot	207
17	HFC0	Tot	12952
18	HFC1	Tot	80
19	HFCA	Tot	285
20	HFCz	Tot	1832
21	HFO	Tot	347
22	HFO1	Tot	5330
23	HFOz	Tot	
24	HHC	Ps	623
25	HHC1	Ps	50
26	HHC2	Ps	
27	HHCX	Ps	2661
28	HHCz	Ps	
29	HNO	Ps	4346
30	HNO1	Ps	3093
31	HNOD	Ps	30
32	HNOz	Ps	5439
33	NDT	Tot	40
34	NDT1	Tot	334
35	SAD	Ps	687
36	SAD1	Ps	519
37	SCE	Pe	209
38	SCE1	Pe	329
39	SST	Tot	544
40	NEC2	Tot	115
41	AQRz	Pw	4029
42	AQR0	Pw	1476
43	HNO2	Ps	16
44	NEC0	Tot	295
45	NAAz	Tot	70
46	XRFz	Tot	30
47	HHCT	PS	
48	NECz	Tot	
49	AQR2	Pw	

Method codes conversion Table for ERF2.2 to ERF 3.2

2.2 METEX first 3 char	2.2 Description	3.2 METCX	3.2 METOA	3.2 METPT
ACD	Acetone/dichloromethane	ACD		
ALK	Alkaline fusion digestion	ALK		
AQR	Extraction with 'aqua regia' (HNO3:HCl = 1:3)	AQR		
EXC	Extraction of organic contaminants by continuous treatment in a Soxhlet or similar apparatus	SOX		
EXH	Separation of organic contaminants from sediment slurries using water steam distillation	EXH		
EXN	Extraction of organic contaminants by shaking with non-polar solvents	EXN		
EXO	Other principles of extraction/separation of organic contaminants from sediment samples. Explain procedure(s) in Plain Language Comment Record(s)	EXO	-	
EXP	Extraction of organic contaminants by shaking with polar solvents	EXP		
HAC	Extraction with acetic acid	HAC		
HCL	Extraction with dilute HCl	HCL		
HFB	As HFC, but with complexation of excess HF with H3BO3	HF-CB		
HFC	As HFO, but with digestion performed in closed vessels (pressurized decomposition)	HF-C		
HFO	'Total' digestion with mineral acids including HF, in open vessels, evaporation of excess HF before analysis	HF-OV		
HHC	Extraction with HNO3, pressure digestion	HNO-CM		
HNO	Extraction with 1:1 HNO3	HNO		
NAA	No extraction: Instrumental neutron activation analysis (total method)	NON	NAA	
NEC	No extraction: Chemical analysis (NTOT, CTOT, etc.)	NON		
NEP	No extraction: Physical analysis (GSAMT, MOCON, LOIGN)	NON	GRV	DFRZ/DOVN/ DRY100/DRY99
PIX	No extraction: Proton induced x-ray emission (total method)	NON	PIX	
SAD	Extraction with a mixture of strong mineral acids without HF (e.g. HClO4 and/or H2SO4 in addition to HNO3)	SAD		
SAN	Slurry method (non-total method)	SAN		
SAT	Slurry method (total method)	SAT		
SCE	Selective chemical extraction of metal species in particulate phases (e.g. by hydroxylamine, oxalate, H2O2, dithionite, ammonium, acetate)	SCE		
SOX	Soxhlet extraction method	SOX	SOX	
SST	Solid suspension technique, ref. M. Hoenig *et al.*, J. Anal. Atom. Spec. 4(1989), 631	SST		
XRF	X-ray fluorescence analysis (total method)	NONE	XRF	

Annex 15: Action points

AGENDA ITEM	ACTIONS	WHO
3	Organise a small group to work intersessionally to evaluate QA information and field data on ratios of contaminants and provide a paper for MON (or other appropriate destination).	Stefan Schmolke
4	Bring to the attention of AMAP the suggestion of WGMS that sediments be considered in more detail in future assessments and that their interpretation could possibly be improved if AMAP adopts OSPAR MON Guidelines and assessment practices, and relevant OSPAR Technical Annexes, for example on normlaisation. A representative of AMAP could attend MON 2007 to observe their assessment methods.	Foppe Smedes
5	Communicate to Andrey Zhilin that WGMS offers to assist PINRO with normalisation of their sediment data.	Foppe Smedes
7	All Members are encouraged to supply any new information on the importance of sediment dynamics for sediment monitoring	All participants
8.1	All participants in PSTS to complete and submit their analyses to RIKZ before May 2007	PSTS Participants
8.2	To present the investigation of the particle affinity and bioavailability of PAHs in relation to coal tar pitch (CTP) using passive samplers at the ASC 2007 in Helsinki	Kristoffer Naes
8.2	All members to consider submission of contributions to ASC 2007 Theme Session J on passive sampling.	All members
8.3	To report back on projects using passivesampling	All involved
10	That national initiatives should seek links between biological effects measurements and passive sampling. .	All participants
10	Bring the possibilities of passive sampling under the attention of national representatives in the ICON steering group	Participants from North Sea contries.
11	Check the completeness of the Guidance document on the use of passive samplers (silicone rubber) in sediment and circulate the final version	Foppe Smedes and Ian Davies
11	Install a website on the use of passive sampling containing information, possiblities and guidance	Foppe Smedes and Ian Davies
12.2	With MCWG, work intersessionally to finalise the guidelines for the determination of alkylated PAHs in sediment	Celine Tixier, Els Monteyne, Lucia Vinas and Ian Davies.
13	Form an intersessional group to develop Patrick Roose's database on contaminant concentrations in sediments from background areas.	Els Monteyne and Carla Palma
13	To collect data to give a wider basis to background values for alkyklated PAH and dibezothiophenes and submit them to the above sub-group.	All participants

Annex 16: Recommendations

AGENDA ITEM	RECOMMENDATION	ACTION
6	To develop a process that gives a more solid base to one-off surveys, taking into account suggestions given under Agenda item 6	OSPAR
8.1	WGMS/MCWG recommends that Kees Booij should join the Coordinating Group for PSTS	PSTS Coord. Group
8.1	To present the work for PSTS and its conclusions at the Theme Session J at ICES ASC 2007 in Helsinki	PSTS Coord. Group
9	Ensure the inclusion of work using DGT in Theme Session J at ICES ASC 2007 in Helsinki.	ICES, Session J conveners
10	That an active role should be sought for passive sampling in the ICON project	Ian Davies and Foppe Smedes to ICON steering group
10	WGMS recommends to encourage all national initiatives that seek links between biological effects measurements and passive sampling.	National delegates
12.1	That the draft Technical Annexes on the determaination of PBDEs and HBCD in sediment be forwarded to OSPAR for adoption.	ICES
12.2	That, when complete, the draft Technical Annex on the determaination of PAHs in sediment be forwarded to OSPAR for adoption.	ICES
13	That the proposed background values for alkyklated PAH and dibezothiophene be forwarded to OSPAR-MON for trial use in assessment	ICES
13	WGMS also recommended that work be undertaken to extend the data set underlying the estimations of the background values for alkyklated PAH and dibezothiophenes	WGMS
15.2	WGMS recommends that QUASIMEME be encouraged to develop a design for an LPS for passive sampling	Foppe Smedes
16	WGMS recommend that they should have their next meeting at IOE, Vigo, Spain around March 2008	ICES
17	WG recommends that the 2008 meeting be chaired by Foppe Smedes, with the assistance of Patrick Roose as Co-Chairman, with the intention that Patrick Roose be invited to take on the Chairmanship after the 2008 meeting	ICES

Annex 17: Proposed Terms of Reference 2008

2007/2/MHCXX The **Working Group on Marine Sediments in Relation to Pollution** [WGMS] (Co-Chairs: F. Smedes, Netherlands, and Patrick Roose*, Belgium) will meet from 31 March to 3 April or from 3 to 7 March 2008 or 25 to 29 February in Vigo, Spain, to:

a) review and comment on the report of the data assessment from the 2007 meeting of OSPAR/MON in relation to sediments;

b) review the application of background concentrations for the following alkylated PAHs in sediments:
   (i) C1-, C2- and C3-naphthalenes;
   (ii) C1-, C2- and C3-phenanthrenes, and;
   (iii) C1-, C2- and C3-dibenzothiophenes, and parent dibenzothiophene;

c) review the background concentrations of proposed alkylated PAHs in sediment in the light of new data supplied intersessionally;

d) review and report on projects that combine biological effects measurements with passive sampling;

e) review the experiences of the use of Guidelines on the use of passive samplers prepared over the last 2 years;

f) evaluate, with MCWG, the results of the passive sampling trial survey (PSTS) for water and sediment collaborative work addressing a) intercalibration, and b) environmental interpretation of the results.

g) receive and comment on national projects involving the use of passive samplers in, inter alia, Norway, Sweden, Belgium, France, and Scotland.

h) review the progress of international cooperative projects involving passive sampling, including the ICON project.

i) receive and comment on reports containing new information concerning the importance of sediment dynamics for sediment monitoring;

j) provide expert knowledge and guidance to ICES Data Centre (possibly via sub-group) as requested;

k) review recent developments in the application of normalisation in the assessment of sediment quality in the Barents Sea;

l) review developments in the use of QUASIMEME information in the interpretation of field data on the ratios of contaminant concentrations;

m) review and report on a survey of metals in North Sea sediments in relation to Background Concentrations carried out by Germany;

WGMS will report by [DATE] 2008 for the attention of the Marine Habitat Committee and ACME.

Supporting Information

PRIORITY:	This Group handles key issues regarding monitoring and assessment of contaminants in sediments.
SCIENTIFIC JUSTIFICATION AND RELATION TO ACTION PLAN:	Action Plan Nos 1.7, 1.10, 1.11, 2.8, and 4.12 a) Anticipating that the report of the proposed 2007 assessment will be available before the meeting, WGMS can review and comment the progress made; b) WGMS 2007 proposed BC values but to strengthen the basis of the values more data need to be collected to evaluation the present values c) New data may warrant the revision of the proposed Background Concentrations d) The combination of passive sampling with biological effect measurements is a strong approach to the coupling of a measure of contaminant exposure and biological effect. It is directly relevant to integrated approaches to monitoring (c.f WKIMON) and to international initiatives on environmental health assessment (e.g. ICON project). e) Guidelines for In Vitro Passive Sampling have been prepared for use in the Passive Sampling Trial Survey and experiences should be collected to further improve and elaborate them. f) This agenda item will review the intersessional progress of the Passive Sampling Trial Survey by WGMS and MCWG and assess whether passive sampling techniques are technically ready for use in the OSPAR monitoring program. An interpretation of the survey data may reveal the usefulness of passive sampling. 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 h) Review by WGMS will contribute to the ICON objectives. i)The annex on Sediment Dynamics for the OSPAR Sediment Monitoring Guidelines (send to ACME) will assist OSPAR and HELCOM, on the incorporation of sediment dynamics in the interpretation of sediment monitoring data. However as new information comes available a revision in future is foreseen and therefore WGMS will continue to collect information and examples on the subject; j)This is in compliance with a continuing requirement from the ICES Data Centre in relation to the development of DOME and associated software k) Cooperation of WGMS members with PINRO in order to normalise data collected by PINRO for grain-size will allow assessment of sediment quality in the Barents Sea in accord with OSPAR guidelines. l)During WGMS 2007, correlations between systematic differences in QUASIMEME data and apparent differences in field data were observed. This led to an intersessional work package that needs to be review during the 2008 meeting m) Receiving a report on a survey carried out by Germany (BSH) on metals in North Sea sediments in relation to Background Concentrations may refresh the view on BC values benchmark for the status of the North Sea concerning metals in sediments.
RESOURCE REQUIREMENTS:	None required.
PARTICIPANTS:	-
SECRETARIAT FACILITIES:	None required
FINANCIAL:	None
LINKAGES TO ADVISORY COMMITTEES:	ACME
LINKAGES TO OTHER COMMITTEES OR GROUPS:	WGBEC, MCWG
LINKAGES TO OTHER ORGANISATIONS:	OSPAR, HELCOM