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Executive summary

The Working Group on Marine Sediments in Relation to Pollution (WGMS) met from 19 to 23 March in Lisbon, Portugal. The meeting was chaired by Patrick Roose and Lucia Viñas and attended by 11 scientists from six countries.

The proposed agenda was accepted without modifications and arrangements were made to carry out the work. Furthermore, a number of informative and relevant presentations were given during the meeting. In particular, information on the use of passive samplers (PS), was presented through this means.

The main task at the meeting was to develop guidance on the design of a regional monitoring programme for contaminants in sediments, an OSPAR request. WGMS reviewed the output of last years' meeting and remained in agreement with the approach outlined.

WGMS understands that EU Member States are most likely to define GES targets for Descriptor 8 on the basis of OSPAR EACs and WFD EQSs. For sediments, these take no account of the physico-chemical characteristics of the tested sediments and hence expressed on total sediment. This implies that, in order to assess sediment conditions against the GES criteria, one needs to sample and analyse total sediments. However, as WGMS continues to focus the monitoring on the fine-grained sediments the impact of this will be limited due to the association of contaminants with the fine fraction. WGMS realises that areas of fine-grained sediment are generally limited which may hamper the overall assessment. However, even within regions that consist of mainly sandy sediments, there will be small sites of accumulation that can be used to characterise the larger system. Concentrating on areas of fine sediment also has the benefit of reducing sampling effort (ship-time) to the most informative areas.

Rather than having an artificial division between inshore and offshore (e.g. 12 km) strata it was considered more appropriate to divide sub-Regions into sampling strata based upon environmental characteristics (e.g. sediment type, sediment dynamics) and existing knowledge on the influence of point source discharges (e.g. the six main rivers that drain into the southern North Sea). The sampling effort required to characterise a sub-Region needs still to be investigated based on actual data. This pertains, amongst others, developing advice concerning division in sub-strata, the representativeness of patches of fine sediments, stratification in relation to point sources and integration of the data. WGMS will, in the first instance, focus on the Southern North Sea as a pilot study that will be handled by a subgroup made up by Patrick Roose, Lucia Vinas, Els Monteyne, Stefan Schmolke, Claire Mason, Rob Fryer, and Maria Belzunce. The final output from the pilot study group will be submitted to WGMS members by the end of January.

In contrast to spatial comparisons against EACs or EQS, WGMS concluded that the best sampling approach for temporal trend analysis of contaminants in sediments is to determine their concentrations in the fine fractions and/or normalise concentrations to a co-factor that reflects the physico-chemical composition of the sediment.

WGMS did not discuss the values that came out of the EAC process to a large extent. They did confirm the futility of values that are orders of magnitude below the current analytical limits and the questionable nature of values that far exceed those currently observed. The group also openly doubted the usefulness of such criteria given the information on which they seem to be based and the values that seem to come out of the different processes. Nevertheless, the group recognises the need to reach conclu-

sions about the health of the marine environment based on the toxicological properties of contaminants. WGMS considers it to be a sad fact that the environmental significance of the observed concentrations can still not be adequately assessed. This situation is particularly deplorable given the great progress that has been made in the area of sensitive and quality assured chemical methods.

WGMS does not consider it to be within its remit to define values for EACs as this is a job better suited for ecotoxicologists.

WGMS discussed the use of passive samplers and passive dosing and suggested, in the light of current experience, that the latter may be a much more promising alternative to the current approaches. The group also recognises this to be a topic on which it can constructively work together with WGBEC and MCWG.

WGMS also identified microplastics to be a scientific issue that can promote cooperation with the other subgroups. The methods to quantify microplastics in sediments are currently not harmonised. WGMS feels that it could contribute in this field given its expertise. Furthermore, WGMS could provide guidance in setting up monitoring programs in sediments.

WGMS decided that the calculated background concentrations for alkylated are fit for use in OSPAR assessments. Further information is expected at next year's meeting and the group will revisit and if necessary adjust the values once the new information has been processed.

1 Opening of the meeting

The 31st meeting of the Working Group on Marine Sediments in relation to Pollution was opened by the Technical Director, Commander Ventura Soares. After a very informative presentation on the Instituto Hydrografico, he welcomed the WGMS and wished everybody a pleasant stay and fruitful meeting.

2 Adoption of the agenda

After briefly going through it, the agenda was accepted without modifications and arrangements were made to carry out the work. As last year, it was clear that agenda item 3 below is a major task and that it would seriously impact the meeting. Given the importance of agenda item 3, it was decided to give it priority at the expense of the other items in the agenda.

3 Spatial design of a regional monitoring programme for contaminants in sediments

WGMS were requested by OSPAR (2011/1) to develop guidance on the design of a regional monitoring programme for contaminants in sediments which can explain whether good environmental status has been achieved on a larger regional scale (e.g. sub-Regions of the OSPAR Regions) within the period 2010–2020, with the major effort in 2014–2020. The guidance should address:

- 1) the selection of areas where monitoring makes most sense, i.e.:
 - a) depths that are sensible to monitor (does it make sense to monitor below 1000 m? 500 m? 200 m? 100 m?);
 - b) sediment types that are sensible to use and the implication for possible spatial coverage;
 - c) ship time considerations;
 - d) time from changes in inputs to response in the sediment can be detected;
- 2) the required spatial resolution of sampling within these areas.

WGMS 2012 reviewed the output of last years' meeting and remained in agreement with the approach outlined. In order to progress with the design task, a GIS approach was used with members of the group providing geographically-referenced data to allow the development and trialling of a design approach developed by Dr Rob Fryer (UK).

Selection of areas where monitoring makes most sense

Compared to coastal and open sea areas, estuaries have unique physico-chemical characteristics that heavily influence contaminant behaviour. Furthermore, estuaries are transitional water bodies rather than coastal waters and thus the MSFD does not apply to them. Estuaries were therefore excluded from consideration within the drafting of the guidelines.

WGMS understands that EU Member States are most likely to define GES targets for Descriptor 8 on the basis of OSPAR EACs and WFD EQSs. For sediments, EACs and EQSs take no account of the physico-chemical characteristics of the tested sediments, but are based upon bioassays of whole sediment (not a given size fraction). Therefore, in order to assess sediment conditions against the GES criteria, one needs to sample

and analyse total sediments. This is not in agreement with current OSPAR JAMP guidelines for temporal trend monitoring that recommend the determination of contaminants in the fine fraction of the sediment (comprised of particles smaller than 63 µm in diameter). An alternative to this approach would be to assume that the EACs were derived based upon a standard sediment composition (e.g. x% TOC, x% Al and y mg/kg Li) and to use these standard conditions to “normalise” the EAC values. Data for contaminant concentrations normalised to sediment composition could then be compared to normalised EACs. This alternative approach was rejected by WGMS because the choice of what is a standard sediment composition could not be agreed, and in some cases normalisation of contaminant concentrations is not appropriate.

WGMS highlighted and agreed that the determination of contaminants in total sediments is very far from being ideal in terms of the scientific understanding of the effects of sediment physico-chemical characteristics on the behaviour of contaminants. However, we are restricted by the way that the GES target is defined (i.e. by comparison to EACs that have been defined without regard to sediment characteristics) and therefore this is the most practical approach. Because finer sediments will have higher contaminant concentrations than coarser ones, the sub-regional assessment of environmental status would be determined largely by the grain size of the sediments analysed, rather than as a result of the anthropogenic component. It is sensible therefore to focus the monitoring on the fine-grained sediments. Even within regions that consist of mainly sandy sediments, there will be small sites of accumulation that can be used to characterise the larger system. Concentrating on areas of fine sediment also has the benefit of reducing sampling effort (ship-time) to the most informative areas.

Rather than having an artificial division between inshore and offshore (e.g. 12 km) strata it was considered more appropriate to divide sub-Regions into sampling strata based upon environmental characteristics (e.g. sediment type, sediment dynamics) and existing knowledge on the influence of point source discharges (e.g. the six main rivers that drain into the southern North Sea). The sampling effort required to characterise a sub-region can then be based upon a risk analysis of existing contaminant information. For example, if a region is comprised of 75% sandy sediment areas and 25% fine sediment area, one could divide it into two sediment type-defined strata, analyse samples from each area and compare the mean (or other appropriate summary statistic) for each area against the EAC. The number of samples collected depends upon the relative “importance” of the areas and the region is assessed as being of GES when concentrations in both areas are <EAC; sampling effort can then be directed according to a risk assessment of existing concentration data compared with the EACs.

If a strata has two or more patches of fine sediment, it could be sub-stratified within those and the mean concentrations weighted according to the proportions of the strata comprised by each sub-strata. Similarly, if you knew you had point sources within a proposed stratum, then would want to sub-stratify it to within and outwith x km of any point source.

Whilst concentrating sampling on the areas of finer sediment, the approach would allow limited sampling of sandy areas to provide reassurance that they are truly <EAC, rather than just relying upon data potentially small areas of fine sediment to characterise large geographical areas.

A further effect of determining concentrations in whole (not sieved) sediment is that there will be more variability in the data than is seen for the temporal trend monitor-

ing on sieved samples and therefore a greater input of local knowledge is required to undertake the design. The use of the mean as the summary statistic for comparison against EAC allows integration of data between strata, nations etc and hence sub-regional assessments. Use of other summary statistics makes this much more difficult.

The baseline sediment type information used in developing the draft sampling design guidelines was drawn from the EMODnet substrate map. This map has a pixel resolution of 2 x 2 km and thus small patches of fine sediment would not have been identified by this procedure, although the EMODnet map was augmented with more detailed information from Cefas for the English section of the North Sea and the Channel.

Initially, areas of fine sediment (defined as being >20% silt-clay) in the southern North Sea and English Channel were identified, and data from ICES DOME was overlaid to show existing CEMP sampling site locations. Belgium and the Netherlands currently use a grid system of monitoring stations that are not concentrated on areas of fine material. Germany has sampling positions that are located to sample sediments from the inflow and outflow areas of the German Bight, plus some additional sites towards the extreme of their territorial waters and also inshore sites designed to observe the impact of the R. Elbe on the German Bight.

Pyrene data from sampling stations within areas of fine sediment were obtained from the ICES database and used to investigate the variability in concentrators in order to inform upon statistical design requirements. These data highlighted difficulties in estimating data variance based upon analyses of different sediment fractions and sampling strategies.

Rob has produced a document that recommends the use of stratified random sampling, concentrating on fine grained sediments. The document provides guidance to countries on how to stratify and how to use local knowledge to produce a sampling design. It is not prescriptive over how many strata or how many samples per stratum are required. Each country should use this Guidance within the next year and report back to WGMS next year on their experience.

How to combine temporal trend and spatial assessments?

The best sampling approach for temporal trend analysis of contaminants in sediments is to determine their concentrations in the fine fractions and/or normalise concentrations to a co-factor that reflects the physico-chemical composition of the sediment. In contrast, for spatial comparisons against EACs, one must determine concentrations in the whole sediment and not normalise.

The environmental status assessment cycle for MSFD is 6 years, therefore a spatial survey of contaminant concentrations in whole sediments is only required once per assessment cycle. These samples could be collected/analysed alongside samples collected for the OSPAR purpose of temporal trend assessments. Alternatively, the sampling could be done routinely but in most years of the assessment cycle the fine fractions would be analysed (for temporal trend assessments) and in one year the whole sediment would be analysed (for spatial assessment against EACs).

Future activities

A subgroup was set up to co-ordinate the Southern North Sea pilot study. This subgroup will be made up by Patrick Roose, Lucia Viñas, Els Monteyne, Stefan Schmolke, Claire Mason, Rob Fryer, and Maria Belzunce. Invitations are to be sent to

Martin Larsen and Andrea Houben ensuring representation from all parties that are involved in the monitoring of this area. The right GIS Information is required, identifying muddy patches and a rationale to select which would be best for monitoring in order to achieve spatial trend aims, i.e. using local knowledge in addition to particle size data to obtain a representative sampling population for the whole region. Additional information on contaminant concentrations that have not been reported to the ICES database will also be required. Rob Fryer will provide a template by the end of April allowing to report this information. This additional information should fall within the identified muddy patches, preferably with total sediment concentrations. If these are not available then information on sieved samples is also acceptable. It is understood that if these are considered as muddy samples, there will be less difference between sieved and total samples. If sieved data is used, it is essential to know the % of fines in the sample. We will aim for each member of the pilot study group to have identified mud patches with supporting rationale by the beginning of September. This will allow consistency of approach from each member to be resolved by the end of September. We will then aim to have the required contaminant concentrations, not present in the ICES database, completed by end of September, allowing sufficient time for Rob to produce a draft design at MIME meeting in December. The final output from the pilot study group will be submitted to WGMS members by end of January.

4 Review and comment on the report of the 2011 meeting of OSPAR/MON in relation to sediments

The meeting of the Working Group on Monitoring and on Trends and Effects of Substances in the Marine Environment (MIME) was held from 5 to 9 December 2010 at ICES in Copenhagen, Denmark. Main issues with respect to sediments, which were discussed during MIME where:

- the integrity of the 2010 monitoring dataset that was used for the annual CEMP assessment.
- the current state of the CEMP assessment
- the related development of the webtool

The summary report of MIME 2011 was available to WGMS and examined with reference to sediments. The report referenced sediments only occasionally, and these were mostly in connection with the work of the Intersessional Correspondence Group on Environmental Assessment Criteria (ICG-EAC). WGMS has conducted a separate review of the output of ICG-EAC under Agenda item 4.

MIME 2011 noted that MEDPOL have recently used the OSPAR methodology for establishing Background Assessment Concentrations (BAC) for sediments and have derived values that are similar to those used by OSPAR.

One agenda item for MIME 2011 was a review of the CEMP. This will be progressed once the advice on sediment spatial monitoring programme design (being developed under WGMS Agenda item 3a) has been received from ICES. Therefore, there is currently no reason for further discussions on this topic.

It was also reported to MIME2011 that QUASIMEME is now accredited as a provider of proficiency testing schemes for the determination of metals, PAHs and PCBs in sediments and biota. Furthermore, it was also reported that QUASIMEME will organise a workshop on determining PFOS in sediments in the second half of 2012.

WGMS noted that there were still problems with the data delivery, a situation that can seriously hamper any activity related to the use of data. Given that the group is often involved in such activities e.g. the use of data from the ICES database for the development of the guidelines, this situation was deplored.

Patrick Roose presented the webtool to the meeting and Dr Rob Fryer (UK) explained the further elaboration of the functionalities of the on-line CEMP assessment application (see <http://dome.ices.dk/osparmime2011/main.html>). The application increases the transparency of the assessment process and gives a fast and convenient overview about the detailed statistical analysis behind it. WGMS welcomed and supports the advances in development and expressed the value of such a tool to improve the communication of the monitoring and assessment results and with this also the motivation of individual parties to contribute to the entire process.

5 Review of Environmental Assessment Criteria

WGMS was requested to review (OSPAR request 2012/2) Environmental Assessment Criteria (EACs) (or equivalents) produced by the Intersessional Correspondence Group on Environmental Assessment Criteria (ICG EAC). This request became somewhat outdated in view of the conclusions reached at HASEC 2012. Nevertheless, the group decided to spend some time on this topic. Patrick Roose gave an overview of the process to develop EACs through OSPAR and the work of ICG-EAC. He also briefed the groups about the outcome of the discussions at MCWG 2012. Craig Robinson, on his turn, informed the group about the outcome of the discussions at WGBEC 2012.

The situation was such that EACs should have been finalised for the 2010 OPAR Quality Status Report (QSR), which proved to be impossible for all compounds. Alternative approaches to assessment criteria were developed at the very last minute allowing an assessment for the QSR. OSPAR recognised the problems associated with this and concluded that a suitable mechanism for the development of EACs was needed. Hence, at the 2010 OSPAR MIME meeting, ICG-EAC was formed, chaired by Patrick Roose, to take this forward and derive new EACs to be used in future assessments.

At that meeting, an approach to produce new EACs was developed and agreed upon based on dose/effect relationships for CEMP and pre-CEMP compounds. Briefly, the EAC is calculated from dose/effect relationship curves, where a level of risk or δ is accepted (suggested to be 10%). The EAC is calculated as the value that corresponds with the lower confidence level of δ . No safety factors would be used, which is different from the approach used to derive Environmental Quality Standards (EQSs) under the Water Framework Directive (WFD). The group agreed to obtain the dose/effect data intersessionally and to apply the method at MIME in 2011.

However, very little data had been obtained prior to the MIME meeting. Therefore it became clear that this approach could not be applied within the timeframe. Values for endpoints were available but the raw data to produce dose/effect curves could not be easily found. Therefore, an alternative approach was considered. A decision tree was drawn up at ICG-EAC. Briefly, if an EQS was available, which is higher than the Background Assessment Concentration (BAC) and considered fit for purpose, this will be used as the EAC. If an EQS is available and less than the BAC then either the BAC needs to be reconsidered or an EAC should be calculated. If no EQS value exists EACs will have to be calculated.

WGMS did not discuss the values that came out of the process to a large extent. They did confirm the futility of values that are orders of magnitude below the current analytical limits and the questionable nature of values that far exceed those currently observed.

WGMS does not consider it to be within its remit to define values for EACs as this is a job better suited for ecotoxicologists.

The group openly doubted the usefulness of such criteria given the information on which they seem to be based and the values that seem to come out of the different processes. The testing of individual compounds spiked into sediments is likely to over-estimate the toxicity of real-world exposures as spiked contaminants are more bioavailable than the same concentration in an aged sediment. On the other hand, contaminants in the environment are present as mixtures and thus comparing environmental sediment concentrations with those of single compound tests does not provide a realistic assessment either. It was even suggested to base further assessment solely on the BC/BAC criteria which are considered to have a much more solid scientific basis. Nevertheless, the group recognises the need to reach conclusions about the health of the marine environment based on the toxicological properties of contaminants. It is a sad fact that the environmental significance of the observed concentrations can still not be adequately assessed. This situation is particularly deplorable given the great progress that has been made in the area of sensitive and quality assured chemical methods.

It will, however, remain extremely difficult to relate lab-observed toxicity data to all the different sediment types that are encountered even without touching upon the issue of normalisation. The chair suggested that using passive samplers is a potential way out of this pitfall that certainly deserves further attention. The idea is to relate both concentrations in the different matrices and toxicity to a common reference matrix. While recognising that this approach may not work for all contaminants and is not an accurate representation of what happens in organisms (particularly those of higher trophic levels), the simple elegance of the approach is certainly appealing. Furthermore, the group recognises this to be a topic on which it can constructively work together with WGBEC and MCWG.

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

WGMS members supplied any available data to further test the recommended normalisation procedure, so that further work could be completed to assess regionalisation of pivot point values and background concentrations. This data needed to include measurements on various fractions for the same sample, preferably for 'pristine' areas. Although more data was presented than in previous years, it was still limited. This is because most laboratories either measure on the sieved fraction (<63µm, <20µm) or total sediment (<2mm). Data was provided by Belgium, France, Germany, Spain and UK. Graphs showing relationships between cofactor and contaminant concentrations were previewed by the WGMS to determine whether the patterns observed match what would be expected, i.e. for higher concentrations of cofactor there are higher concentrations of contaminant.

Last year we showed that pivot point values could vary regionally, and although we have not had enough time to compare this new dataset to BACs, most of the relationships checked showed the expected trend, that is higher concentrations in the cofactor and contaminant in the finer fraction (<63µm) sediment (Figure 1). However,

there were some cases where it is clear there was not the expected relationship between cofactor and contaminant (Figure 1– sample from Spain – known to be caused by small plant material).

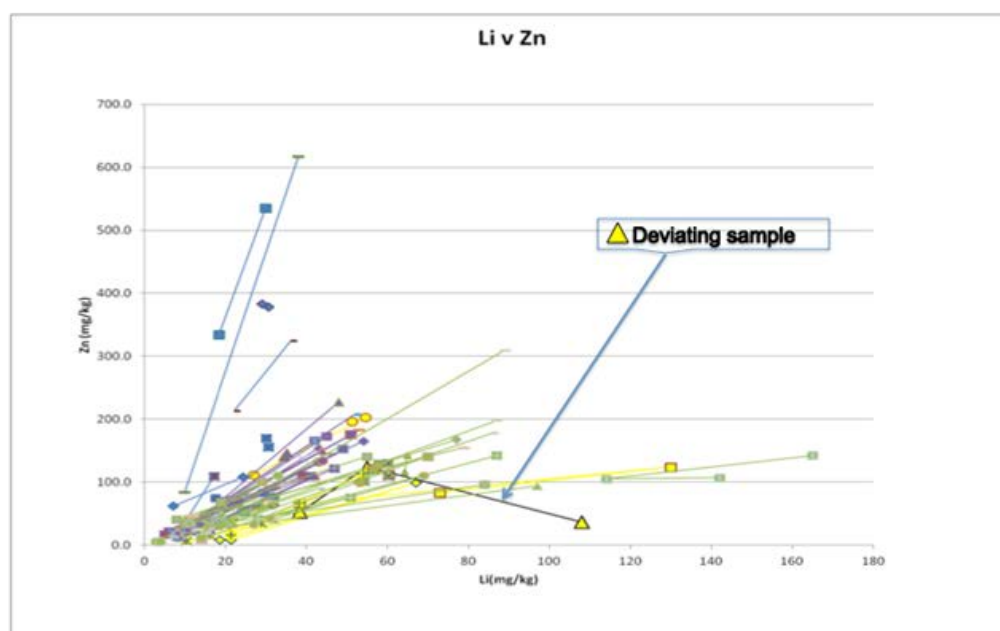


Figure 1. Correlations between lithium and zinc for sample data provided to WGMS at its 2012 meeting, illustrating that for most samples the expected and required positive relationship for pivot point normalisation is there. One sample (S3, yellow triangle) deviates from this and normalisation using this cofactor would in this case not be sensible.

7 To continue work on the uncertainty in data assessments arising from the selection of cofactors

Further work was also required to assess the normalisation procedure with regards to selection of co-factors. Examples are given in the trace metals baseline study below of where further normalisation (after sieving) does not further improve variability in data were presented at the meeting and discussed.

Members all agreed that before completing trend assessment using geochemical normalisation it is important to check the relationship between cofactor and concentrations, and make sure that it reduces variability in the concentrations.

In order to complete temporal assessment, all CPs should submit raw data for temporal trend monitoring including cofactor concentrations. The normalisation procedure advocated by WGMS and defined in the JAMP guidelines (OSPAR, 2002) will be followed for temporal trend assessment. If CPs feel that the temporal trends produced are incorrect for their region/subregion because of inappropriate application of the normalisation procedure, i.e. the normalisation has made the variability worse than if normalisation had not been applied, or different pivot point and/or BAC are different for their regions, then they will need to appeal to OSPAR MIME, supplying evidence to demonstrate this is the case. If such cases arise MIME may then refer to WGMS for advice to ascertain the validity of these cases. Evidence must be from a spatial spread representative of the region concerned, show repeatability and have associated quality assurance data.

Claire Mason presented final results from the trace metal baselines study for England and Wales completed last year to help with disposal site assessment. The main aim for this project was to produce regional baselines as when comparing disposal site concentrations with the OSPAR BACs most of them were higher than these, and it was difficult to assess impact at sites. The recommended OSPAR normalisation procedure (sieving at 63µm, and then completing further geochemical normalisation using cofactors) was tested using correlations of metal concentrations against various geochemical cofactors, and checking standard deviation between normalised values for a region against raw values. Results from these tests showed that further normalisation of the sieved concentrations did not reduce variability and so no further normalisation was necessary. Four baseline approaches were evaluated. The resulting baselines are comparable with the OSPAR BACs, and reflect that while regionally there are differences in metal baseline concentrations overall they match well with OSPAR BACs (C. Mason *et al.*, 2012 in publication, Evaluation of regional baseline approaches of trace metal concentrations for disposal site assessment in England and Wales).

Reference

OSPAR, 2002, JAMP Guidelines for Monitoring Contaminants in Sediments (agreement 2002-16), OSPAR Commission, London, UK.

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

8.1 Develop of background concentrations for alkylated PAHs in sediments

During WGMS 2007 background concentrations for some alkylated PAHs in sediments were developed using relatively few data on these contaminants then available from France, Scotland and Norway. The French data were from sediment cores in the Bay of Biscay, and were available in the database. Data from home laboratories in Oslo and Aberdeen were also obtained. The Norwegian data were from areas on the west coast, whereas the Scottish data were from the UK National Marine Monitoring.

During the present meeting, WGMS received data on PAHs in dated sediment cores from South-Western Barents Sea and North-Eastern Norwegian Sea. The samples have been collected in 2006–2010 by the Institute of Marine Research (IMR), Bergen, Norway, and Norwegian Geological Survey (NGU), Trondheim, Norway, under national MAREANO program of mapping the seabed of the Norwegian shelf, and analysed for hydrocarbons at IMR and for TOC at NGU. The cores have been dated as deep as possible at DHI, Denmark.

These Norwegian data were treated as follows:

- 1) The deepest layer of the core was selected in all cases.
- 2) 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, half of the DL was taken into the sum.
- 3) Similarly for the rest of the alkylated Naphthalenes: 3 dimethyl naphthalenes were summed to give NAPC2 for cases where no NAPC2 was reported, 3 trimethyl naphthalenes were summed to give NAPC3 and 2 individual tetramethyl naphthalenes were summed to give NAPC4.

- 4) In the case of alkylated phenantrenes 4 monomethylphenantrenes were summed to give PAC1, 4 dimethylphenantrenes to give PAC2, 3 trimethylphenantrenes to give PAC3 and the value of 1,2,6,9-TetraMethylPhenanthrene was used for PAC4.
- 5) For alkylated Chrysenes the value of 1-Methylchrysene was taken as CHRC1, the value of 6-EthylChrysene as CHRC2 and the value of 6PropylChrysene as CHRC3.
- 6) Similarly, for alkylated Dibenzothiophenes the value for 4-Methyl-Dibenzothiophene was used as DBTC1, the value of 4-Ethyl-Dibenzothiophene as DBTC2 and the value of 4-Propyl-Dibenzothiophene as DBTC3.
- 7) In all cases, if the values were <DL, half of the DL was taken into the sum.

WGMS received information on the content of parent and alkylated PAHs for 85 cores but only TOC information for 18 of them.

As a first step, the sum of the different groups of alkylated PAHs was calculated and the median of all the cores was determined. The results are tabulated below.

Table 1. Median of the different groups of alkylated PAHs calculated from 85 cores from Norway (expressed as µg/kg d.w).

Parameter	Concentration (ug/kg dry weight)
NAPC1	5.5
NAPC2	11.1
NAPC3	3.8
NAPC4	2.3
PAC1	8.7
PAC2	3.8
PAC3	2.5
PAC4	0.3
DBT	0.7
DBTC1	0.6
DBTC2	0.3
DBTC3	0.3
CHRC1	0.3
CHRC2	0.3
CHRC3	0.3

As TOC values were only available for 18 cores, these cores were selected and the concentrations of the different groups of alkylated compounds were calculated as explained before but with results normalised to 2.5 % TOC. The median of each group was then determined.

Apart from the data from Norwegian cores, the data of some of the groups of alkylated PAHs for the two French cores from the Bay of Biscay were still available. Given that in this case the results were reported as groups of alkylated PAHs, no more calculation was needed. The PAC1, PAC2 and PAC3 results derived from these cores were initially reported as PH/ANTC1, PH/ANTC2 and PH/ANTC3 respectively. These results were also normalised to 2.5% TOC taking into account their TOC content. Again, the median of the cores was determined.

It was decided not to use the rest of the information in the database as they were not derived from deep core.

Finally the median of the medians of the two sets of data was determined and the final results are given in the table below. In order to compare these values with those proposed in 2007 these values are also presented in the table.

Table 2. Proposed Background Concentrations for alkylated PAHs in sediments, expressed as concentrations normalized to 2.5% organic carbon.

Parameter	Proposed in 2007 (ug/kg dry weight, normalized 2.5% TOC)	Concentration (ug/kg dry weight, normalized 2.5% TOC)
NAPC1	1.7	16.8
NAPC2	2.3	27.4
NAPC3	5.0	8.7
NAPC4		5.4
PAC1	4.5	27.8
PAC2	8.3	12.0
PAC3	9.9	7.0
PAC4		1.6
DBT	1.3	2.6
DBTC1	2.3	1.8
DBTC2	5.0	1.6
DBTC3	4.8	1.4
CHRC1		1.8
CHRC2		1.4
CHRC3		1.1

On the basis of the information presented during the meeting, WGMS decided that the calculated background concentrations in the second column of the table above are fit for use in OSPAR assessments. Further information is expected at next year's meeting and the group will revisit and if necessary adjust the values once the new information has been processed.

8.2 Develop of background concentrations for dioxins and related substances

Up till now, no information has reached the group concerning levels of dioxins and related substances in dated sediment cores. Prof. Dr. Ingemar Cato was able to present the results of a Swedish study on this topic to the group. The latter describes background concentrations of PCDD/F observed by Professor Ingemar Cato (Göteborg University, Sweden) and co-workers in two sediment cores from the Gulf of Bothnia and one core from SW Baltic Sea. The results show that very low concentrations occur in these prehistoric fine-grained sediments. The WHO-TEQ2005 in fine-grained sediments seem to vary between 0.23 and 1.5 pg / g dw with a mean of 0.66 ± 0.73 and a median of 0.24 pg/g dw. The full paper is attached to the report as annex 6.

It is unadvisable to suggest background concentrations based on this study alone. However, the values in this study can already be considered as indicative for the background level of dioxins. More information of the same type would allow to coming up with a better number.

9 Passive sampling

9.1 Start work on a review of the use of passive sampling for measurements in sediments and approaches to the estimation of pore water concentrations

WGMS still is of the opinion that such a document would indeed be very interesting and potentially useful. A review of passive sampling measurements in sediments and approaches to the estimation of pore water concentrations is currently still missing.

Possible content:

- Preparation of a list of passive sampling devices that may be used for a range of measurements of bioavailable contaminants in sediments.
- Provide a description and some general guidelines for the adequate implementation of these tools for various measurements.
- Experiments for the measurements of pore water concentrations or the measurement of the entire bioaccessible fraction using an infinite sink approach.
- Measurement of diffusive fluxes and concentration gradients between overlying and pore waters.
- The importance of black carbon and other amorphous organic matter phases in the often high apparent sediment-pore water partitioning observed in sediments.
- The use of passive sampling data for assessing the status of the marine environment. This will require the development of assessment criteria that provide the same level of protection as EQS.

WGMS aims to further develop this into a guideline fit for OSPAR or other purposes and one or several ICES TIMES papers. This work should cover both organics and metals. WGMS expects to need 3 years to complete this work. WGMS will seek active collaboration on this topic with MCWG and WGBEC.

9.2 To continue the work on passive sampling as a proxy for partition coefficients for organic contaminants in sediments

There is no incentive to continue work on this topic and no new information was made available at the meeting. WGMS decided that this topic should no longer be part of the agenda.

9.3 Report ongoing and new projects involving passive sampling

9.3.1 Update on use of passive samplers in UK

Craig Robinson presented an update on passive sampling and passive dosing projects in the UK.

In the last few years, the UK marine Competent Monitoring Authorities have worked on a number of projects related to passive sampling of the marine environment. The most notable was the UK passive sampling survey of coastal waters that was co-ordinated by Cefas and reported to Defra in 2011 (Balaam *et al.*, 2011). That project integrated the use of different types of passive sampler (silicone rubber, semi-permeable membrane device, diffusive gradients in thin films) and included deployed mussels to investigate the presence and extent of contamination from hydrophobic, polar and metallic compounds in the water phase. The project developed expertise and capacity and has led to further and on-going investigations into the use

of passive samplers as surrogate biota for use in WFD trend monitoring by the environment agencies and as a screening tool for monitoring presence of emerging contaminants in marine and estuarine waters by Cefas. Working via a PhD studentship, Marine Scotland Science are continuing to develop the integration of passive sampling of aquatic environments with novel passive dosing and in vitro toxicity tests with passive sampling and aim to extend this project to investigate the feasibility of this approach to assessing sediment toxicity. The use of passive sampling as a tool to inform upon the suitability of dredged spoil material for marine disposal is also being investigated. The passive dosing platform being utilised is the silicone rubber o-ring approach described by Smith *et al.* (2010). To date the project has focussed on a river catchment in NE Scotland, with sampling sites from the headwaters to the estuary. Current work is expanding this work into the marine environment, with sampling sites along a pollutant gradient in the Firth of Forth; future work will apply the passive sampling/passive dosing approach to sediments. Within the river catchment the project has investigated the relationship between freely dissolved PAH and PCB concentrations, the environmental presence of polar herbicides and pesticides, and the cytotoxicity (neutral red uptake) and cytochrome P450 (EROD)-induction potential of silicone rubber passive sampler extracts to a rainbow trout liver cell-line (RTL-W1). In addition, partition and diffusion coefficients are currently being determined in order to allow the use of silicone rubber PS to determine aqueous freely dissolved concentrations of semi-polar pesticides and herbicides that have been shown to be accumulated by silicone rubber samplers. On-going validation of the passive dosing system is using passive dosing of PAH compounds loaded onto silicone rubber o-rings and use of cytotoxicity and EROD endpoints in RTL-W1 cells. Integration of chemical characterisation with other toxicity endpoints is also being developed, including algal growth inhibition.

References

- Balaam, J. *et al.*, 2011. The Use of Passive Sampling for Monitoring Offshore Waters. Report to Defra.
- Smith, K.E., Oostingh, G.J., Mayer, P. 2010. Passive dosing for producing defined and constant exposure of hydrophobic organic compounds during in vitro toxicity tests. *Chem. Res. Toxicol.*, 23, 55-65.

During the discussion Patrick Roose raised the question if passive sampling technique can be considered to be a mature technique. According to Craig this is the case in terms of environmental monitoring, but this was not the case yet in terms of regulatory monitoring. The latter is mainly because of the basis upon which current EACs are defined, i.e. total water concentrations and not the bio-available fraction or total dissolved concentrations. He is also not pleased with the current EACs and suggests it would be better if these were based on environmentally relevant concentrations such as freely dissolved concentrations.

Claire Mason commented that the DGT passive sampling project presented last year by Thi Bolam was continuing. This work was mainly to aim at validating the DGT method at impacted disposal sites. Further sediment cores were collected (in triplicates) in June 2011 at sea for DGT passive sampling at Souter Point disposal site, aiming at a dredge impacted site, a capping site and a reference site. Direct deployment of DGT probes into sediments was not practical for this sampling episode, but instead the cores were collected and incubated at sea. The DGT probes were inserted into the sediment for 24 hours (less time than in the previous year as there were greater time restraints at sea than when completing in the laboratory). Oxygen profiles of the cores

were completed prior to DGT deployment and post DGT retrieval. Comparable results were achieved to last year, although the method was less sensitive to some metals (e.g. cadmium) due to short exposure time. The cores were then sliced at 1cm intervals, and analysed for chlorophyll, porocity, PSA, and organic carbon. Additional parameters that may be measured include trace metal concentrations in the sediment layers to compare with the metals measured in the calculated pore water (from DGT probe). Reporting on this work will be completed in 2012/2013.

9.3.2 Update on use of passive samplers in Spain

Maria J Belzunce presented the work that has been done up to day in the Marine Research Division of AZTI-Tecnalia related with passive samplers. The first objective was to probe the applicability of Diffusive Gradient in Thin-Films (DGTs) for metal trends monitoring in estuarine and coastal waters. This study was carried out in 13 estuaries of the SE of the Bay of Biscay. The estuaries are different in their morphology and hydrodynamic. In situ deployment of DGT devices was done in the inner and outer part of the estuaries to cover a wide salinity gradient. The devices were deployed during about ten days. Metal concentrations accumulated in the DGTs were analysed in the laboratory by AAS. The comparison of the results obtained by DGTs with the historical data series of filterable-metal concentrations in these estuaries highlights some advantages of the first. DGTs accumulate constantly in situ, representing the time-averaged concentration of trace metals during the deployment time, and therefore better reflect the fast changes of water metal concentrations in highly dynamic estuaries. On the other hand, saline matrix effects are overcome (nitric acid extraction) and the metals are concentrated, increasing the sensitivity of analyses.

A second objective was to evaluate the applicability of techniques based on the labile fraction of contaminants to characterize the impact of an effluent plume. For this purpose 12 stations were chosen along the Oiartzun estuary (south eastern Bay of Biscay) and water quality was assessed by DGTs. Also, at the outermost stations, located inside the harbour domain, in situ sea-urchin bioassays (48 h) were performed and water samples were collected during a tidal cycle. In the laboratory, composite water samples were evaluated by the sea-urchin bioassay and Toxicity Identification and Evaluation procedures (TIEs) were applied to identify the chemicals responsible of the observed toxicity. TIEs consist on the physical/chemical manipulation of samples to reduce the bioavailability of specific contaminants and to establish cause-effect relationships. A decrease in metal concentrations, as measured by DGTs, from the inner riverine stations to the mouth of the estuary was observed. Paralelly, an increase in the survival of sea-urchin larvae in situ and laboratory bioassays were detected. Additionally, metals were identified as the contaminants responsible of the observed toxicity by means of TIEs.

On basis the obtained results, DGTs seem to be a promising tool for metal trends monitoring in highly variable systems and for the assessment of potential toxicity of effluents in the aquatic environment.

The next objective is to develop environmental quality standards for passive samplers or "correction factors" to compare spot sampling results to those from DGTs.

During the discussion Craig Robinson pointed out that it was not clear yet which metal was responsible for causing the toxicity. He also mentioned that the measured concentrations seemed to be very low in comparison with the WFD-EQS because they

were measured in the dissolved phase and not in total water. Ingemar Cato noted that the techniques seem to work very well.

Maria was also asked to consider the applicability of passive sampling as a mature technique. According to her, the picture you get with passive sampling is much more realistic than when measured with classic spot sampling. The DGT-PS also detects quick changes in the environment. It is furthermore a very useful technique for use in bioassays. In future research, EQS-values will be developed based on DGT-measurements. Patrick Roose stated that Maria showed very interesting results with DGT-PS and emphasised the importance of the work done. This technique seems to be the way forward for metal monitoring.

Craig Robinson noted that no PRCs were used in the DGT technique to compensate for environmental factors like temperature and hydrodynamics. Patrick Roose suggested that we should change our way of thinking on this. There is no interest in making matters too complicated. The uptake as it is, is interesting because it gives an idea of the pollution pressure, making it a relevant measurement in its own right. Claire Mason pointed out that we need the PRCs to standardize in order to be able to compare concentrations between different locations. But perhaps this is not really necessary if you look at pollution pressure as such. In fact, we also tend to ignore the same factors, such as water circulation, that may equally be the cause for differences in the levels in biota. The discussion led to the conclusion that this more straightforward approach would possibly depend on the compound you are looking at, specifically the form in which it causes toxicity.

Víctor M. León presented the preliminary results of a study that compared the efficiency of two integrative samplers (the semipermeable membrane device, SPMD and the continuous flow integrative sampler, CFIS, designed by Labaqua S.L.) in marine coastal waters.

The study area was a Mediterranean coastal lagoon (Mar Menor lagoon), close to one of the main areas of intensive horticulture in Europe, the Cartagena Field basin. Furthermore, the Albuñón watercourse is the most important trap of the Cartagena Field basin and drains into the Mar Menor. Finally, the area has a seasonal pressure by tourism.

The samplers were immersed for 8 days at 4 sampling points of which 2 were affected by the Albuñón and the rest in more representative marine areas. CFIS and SPMD were applied in duplicate and triplicate at several sampling points. The SPMD appears to be affected by turbulence and temperature and requires the use of performance reference compounds (PRC). In the case of The CFIS, the sampling rates are independent of turbulence, because flow is constant, but PRCs are also required in order to compensate for temperature effects.

The mean concentrations obtained with both sampling devices were compared with the daily concentration of pollutants (2 samples per day) determined by SBSE/GC/MS. Significant daily differences were observed in the input of organic pollutants (nonylphenols, PAHs and pesticides) from the Albuñón. The sampling devices situated in its area of influence appear to be exposed to extremely variable levels.

The repeatability of the obtained results was satisfactory (lower than 20% for the majority of cases). CFIS show more accurate mean concentrations for PAHs than SPMD in the more stable areas, i.e. where the fluctuations of pollutant concentrations are lower and physicochemical properties vary less. SPMD concentrations corresponded slightly better with mean spot values than CFIS in high variable conditions. CFIS has

proved adequate for nonylphenols and chlorpyrifos in all sampling areas. Also, CFIS showed better overall results in the sampling points that are considered to be representative for the marine area. Nonetheless, more data are required to complete the evaluation of both sampling devices. This study took place in spring, and should be backed up by the results of an analogous one performed in autumn of which the results will soon be available, courtesy of the Spanish Inter-Ministerial Science and Technology Commission through "DECOMAR" project (CICYT, CTM2008-01832).

During the discussion Craig Robinson asked if the water that they analyzed was filtered. Apparently, filtration was not necessary due to the use of twisters (PS) as an analytical technique. Patrick Roose inquired about the preference of SPMDs over PDMS passive samplers. According to Victor, PDMS were selected because they seem to be able to accumulate a lot of compounds. Also, they were not familiar with PDMS up till recently and less able to predict their performance in the different environmental systems, hence the choice of SPMDs. Craig pointed out that a PDMS based PS was also used in continuous flow integrative samplers. He was also interested in the outcome of a study aimed at developing a continuous flow PS in Belgium, the latter in collaboration with Marine Scotland. Patrick Roose explained that the design of the sampler was finalized. It is based on the movement of waves to pump water through the system, avoiding the use of batteries or another power supply. The idea is certainly very interesting, but no money was available yet to build a prototype.

9.3.3 Update on use of passive samplers in Belgium

Els Monteyne presented work done in Belgium on integrated passive sampling with PDMS-strips during the project INRAM.

For 4 subsequent years polydimethylsiloxane (PDMS) passive samplers were deployed in the 3 major harbours in Belgium and at sea. The sheets were analyzed for PAHs and PCBs, priority pollutants for OSPAR, the WFD and presumably the MSFD. With the use of the performance reference compounds (PRCs), sampling rates were calculated and water concentrations were determined. The sampling rates were calculated using the PRC-data of PAHs and PCBs together and by modelling the dissipated PRCs to the equilibrium constant of the PRC between water and the passive sampler. Individual concentrations of PAHs varied from 0.01 to 67 ng/L, while for PCBs these varied from 0.01 to 0.45 ng/L. Sum 10 PAHs were between 5.43 and 194 ng/L. For PCBs concentrations were much lower and sum 14 PCBs was between 0.03 to 1.64 ng/L. Sampling rates seem to vary according to hydrodynamic circumstances and amount of bio-fouling. In the harbours the sampling rate was lower, varying from 1.00 L/d to 5.08 L/d; while in open sea the sampling rate was reached up to 14 L/d. The samplers showed a difference in pollution pressure between the harbours, as well as within the harbours. The sampling station at open sea was clearly less polluted than stations situated in the harbours. Comparison of PAH-patterns showed a flux from the harbours to the open sea station. Also PAH-patterns in one station were consistent over the years. Stations at yachting clubs showed highest pollution pressure, which proves that they are a possible source of pollution. Passive samplers were deployed simultaneously with mussels and oysters. Results show good agreement with former published modelling of passive samplers and mussels by Booij *et al.* (2006). Samplers that were deployed in the stations, were used in toxicity tests as passive dosing devices. These results show a link between actual environmental measurements and toxicity. To conclude passive samplers seem to be a very powerful tool for monitoring hydrophobic pollutants and linked to eco-toxicological assessment

criteria, passive samplers could be the answer to current problems in monitoring of the marine environment.

Reference

Booij *et al.*, 2006. Environmental monitoring of hydrophobic organic contaminants: The case of mussels versus semipermeable membrane devices.

During the discussion in the group, Patrick Roose again pointed out that we should alter our way of thinking about the use of passive samplers. Instead of trying to relate to concentrations we should focus on measuring pollution pressure in the environment as such. The link between the toxicity tests with passive dosing and passive sampling measurements is unique. Here, toxicity and levels are measured for the same medium and that medium can be related to all the other media in the environment.

Given the difficulties that exist to come up with relevant assessment factors, the worry exists that the classical approach to monitoring will not give us the right answers in terms of environmental assessment. On the other hand, passive sampling could provide an answer to this and is at least a promising way to achieve integrated monitoring.

The group agreed that the technique indeed seemed to be very promising to work with in different areas of environmental monitoring.

Claire asked what future perspectives are for the research in passive sampling following the INRAM project. Patrick Roose answered that a follow-up project is planned provided that the necessary funding can be found. The research would be more directed towards a holistic view on the relation between the environmental systems regarding pollutant partitioning. Partitioning in the broadest sense seems to be purely driven by physico-chemical processes. An article on this topic written by Michiel Claessens will appear later this year.

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

No questions were submitted to the group.

11 Miscellaneous

11.1 Evaluate potential for collaboration with other EGs in relation to the ICES Science Plan and report on how such cooperation has been achieved in practical terms (e.g. joint meetings, back-to-back meetings, communication between EG chairs, having representatives from own EG attend other EG meetings)

WGMS has been collaborating for many years with MCWG (Marine Chemistry Working Group) in the development of technical annexes, and will continue to do so in the future. WGMS is of the opinion that it can collaborate with MCWG in any field where (novel) techniques or developments related to contaminants in sediments are brought forward.

Several attempts to cooperate took place in the past:

- In 2003 in Tromsø 2 members of the WGMS participated in the WGBEC meeting;

- In 2006, there was a plenary session between WGMS and WGBEC, and between WGMS and MCWG in Copenhagen.

Also, some members participate in both WGMS and WGBEC or MCWG.

The topic was discussed earlier at MCWG and WGBEC. Patrick Roose (MCWG) and Craig Robinson (WGBEC) presented the outcome of these earlier discussions.

WGMS welcomed the suggestion to have a joint meeting with both groups at the ICES headquarters in 2014 and is convinced of the importance and need to have such a meeting.

WGMS identified the subject of passive sampling, in particular, as the topic for collaboration between the three groups. It envisages the development of a holistic approach to monitoring based on this technique combining measurements in sediment and water with passive dosing. Particularly the latter is still in full development and results seem to be promising. WGMS thus identified passive sampling as a scientific issue that can promote cooperation with the two other EGs:

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

WGMS also identified microplastics to be a scientific issue that can promote cooperation with the other subgroups. Microplastics are microscopic particles of plastics that result from the fragmentation of plastic debris at sea. These microplastics have persistent properties that can become dispersed in the marine environment through hydrodynamic processes and ocean currents and have adverse effects on marine life. However, these adverse effects cannot entirely be assessed as yet. The methods to quantify microplastics in sediments are also not harmonised. WGMS feels that it could contribute in this field given its expertise. Furthermore, WGMS could provide guidance in setting up monitoring programs in sediments.

11.2 Deliberations about the future organisation of ICES EGs

Patrick Roose presented the group with the vision of SCICOM on how to organise the work of EGs in the future. Given the nature of its work, WGMS does not think it will have much difficulties to justify its work in the immediate future but thinks that this may effectively limit valuable contribution of members in the long run and hence endanger continuation of the work and the group. The group is fully in line with the opinion of its former chair, Foppe Smedes, stating that:

“An efficiency step is not expected with shortening the life of EGs. I think it is the family feeling born in the continuous groups that gives the often excellent outputs. Disappearance of the continuity may negatively influence the participation.”

12 Recommendations and Action list

The actions and recommendations are listed in Annexes 4 and 5.

13 Chair(s) for 2013

Patrick Roose and Lucia Viñas will continue to act as chairs for the time being. At the next meeting of WGMS in 2013, new arrangements for chairmanship will have to be made.

14 Date and venue of the next meeting

WGMS is kindly invited by Claire Mason to have its 2013 meeting in Lowestoft. The date needs to be set so that it doesn't conflict with MCWG, and, if possible, coincides with WGBEC!

15 Closure of the meeting

The meeting was closed on Friday, 23 March 2011 at 12h30. Both Chairs thanked the group for their collaboration to a successful meeting and thanked, on behalf of the entire group, Carla Palma and her colleagues for hosting the meeting in such an outstanding way.

Annex 1: List of participants

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Annex 2: Agenda

The **Working Group on Marine Sediments in Relation to Pollution** (WGMS), chaired by Patrick Roose, Belgium, and Lucía Viñas, Spain, Lisbon, Portugal, 19–23 March 2012:

1. **Opening of the meeting**
2. **Adoption of the agenda**
3. **Sediments monitoring**
 - a. Develop guidelines for Spatial design of a regional monitoring programme for contaminants in sediments; (OSPAR request 2011/1)
To develop guidance on the design of a regional monitoring programme for contaminants in sediments which can explain whether good environmental status has been achieved on a larger regional scale (e.g. sub-Regions of the OSPAR Regions) within the period 2010-2020, with the major effort in 2014-2020. The guidance should address:
 - 1) the selection of areas where monitoring makes most sense, i.e.;
 - (i) depths that are sensible to monitor (does it make sense to monitor below 1000 m? 500 m? 200 m? 100 m?);
 - (ii) sediment types that are sensible to use and the implication for possible spatial coverage;
 - (iii) ship time considerations;
 - (iv) time from changes in inputs to response in the sediment can be detected;
 - 2) the required spatial resolution of sampling within these areas.

The guidance should be divided into coastal and open water (i.e. beyond 12 nautical mile limit) and take into account the need to distinguish between point source monitoring and diffuse sources.
 - b. Review and comment on the report of the 2011 meeting of OSPAR/MIME in matters concerning sediments;
 - c. Review further information relevant to the regionalisation of pivot values and background concentrations of contaminants in sediment;
 - d. To continue work on the uncertainty in data assessments arising from the selection of co-factors.
4. **Background concentrations**
 - e. Review of Environmental Assessment Criteria or equivalents (OSPAR request 2012/2)
To review scientific robustness and update, as necessary, EACs or equivalent effects levels calculated for CEMP and pre-CEMP determinands.
 - f. Continue collection of data and develop background concentrations for alkylated PAHs.

5. Passive Sampling

- g. Start work on a review of the use of passive sampling for measurements in sediments and approaches to the estimation of pore water concentrations;
- h. To continue the work on passive sampling as a proxy for partition coefficients for organic contaminants in sediments;
- i. To report on ongoing and new projects involving passive sampling.

6. Miscellaneous

- j. Provide expert knowledge and guidance to ICES Data Centre (possibly via subgroup) as requested.
- k. Evaluate potential for collaboration with other EGs and other ICES initiatives in relation to the ICES Science Plan and report on how such cooperation has been achieved in practical terms (e.g. joint meetings, back-to-back meetings, communication between EG chairs, having representatives from own EG attend other EG meetings).

Annex 3: WGMS terms of reference for 2013

The **Working Group on Marine Sediments in Relation to Pollution** (WGMS), chaired by Patrick Roose, Belgium, and Lucia Viñas, Spain, will meet in Lowestoft, UK, March 2013 (TBA) to:

Sediments monitoring

- a) Finalise the development of guidelines for Spatial design of a regional monitoring programme for contaminants in sediments
- b) Review and comment on the report of the 2011 meeting of OSPAR/MIME in matters concerning sediments

Background concentrations

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

Passive Sampling

- d) Initiate a review on the use of passive sampling for measurements in sediments in relation to assessing the state of the marine environment
- e) To report on ongoing and new projects involving passive sampling

Miscellaneous

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

WGMS will report by 15 April 2013 (via SSGHIE) for the attention of SCICOM and ACOM.

Supporting Information

Priority	This Group handles key issues regarding monitoring and assessment of contaminants in sediments.
Scientific justification and relation to action plan	<p>a) This is a direct request from OSPAR.</p> <p>b) Anticipating that the report of the proposed 2012 assessment will be available before the meeting, WGMS can review and comment the progress made;</p> <p>c) Background values play an important role in the OSPAR assessments of contaminants in sediments. WGMS has proposed background concentrations on available information. However, the amount of available data is sparse. Additional information is expected and may warrant revision of the proposed background concentrations (OSPAR request 3, 2007) WGMS will review new information for the further development and advise accordingly.</p> <p>d) Passive samplers are increasingly used in environmental monitoring, but the approaches and methodologies differ. A document focussed on their use in sediments, discussing the different type of passive samplers and their use, is envisaged. The group would particularly like to develop the use of passive sampling as a tool to assess the good environmental status of the marine environment.</p> <p>e) 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.</p> <p>f) Response to internal ICES requests.</p>
Resource requirements	None required
Participants	The Group is normally attended by some 15 members and guests.

Secretariat facilities	None
Financial	No financial implications.
Linkages to advisory committees	ACOM
Linkages to other committees or groups	WGBEC, MCWG
Linkages to other organizations	OSPAR, HELCOM

Annex 4: Recommendations

Recommendation	For follow up by
1. WGMS recommends that the proposed BC for dioxins is used for OSPAR assessment purposes pending the availability of additional information.	ACOM, OSPAR
2. WGMS recommends that the proposed BC for alkylated PAHs is used for OSPAR assessment purposes pending the availability of additional information.	ACOM, OSPAR
3. WGMS that OSPAR continues to use the current normalisation procedure for temporal trend assessment. WGMS recognises that the procedure will not work in particular situations and recommends that contracting parties provide sufficient evidence for this to the appropriate OSPAR level. WGMS is happy to assist in evaluation the provided information when and if it becomes available.	ACOM, OSPAR
4. WGMS recommends that WGBEC are invited to advice on the suitability of sediment GES targets for contaminants having specific regard to sediment composition e.g. grain size, type of organic matter.	ACOM, OSPAR
5. WGMS recommends that WGMS, WGBEC and MCWG meet at the ICES headquarters in 2014 and organize a joint session	WGMS, WGBEC, MCWG

Annex 5: Action list

Agenda item		
3a	Collate all available concentration data for the Southern North Sea from the last decade and use it to propose a sampling design.	Rob
3a	Collate GIS information for the Southern North Sea with emphasis on identifying the patches of fines that will become the target population of the pilot study in December.	Claire (coordination) and all members
3a	Collate GIS information for the entire OSPAR area with emphasis on identifying the patches of fines that will become the target population of the pilot study at the next meeting of WGMS.	As above
3a	To apply the outcome of the pilot study for the other OSPAR subregions for evaluation at the next WGMS meeting.	All members
3a	Develop a sampling design that allows assessing good environmental status for the Southern North Sea as a pilot for the development of an OSPAR guideline. The envisaged time table is as follows: Provide information on the proposed mud patches (sampling population) by the start of September Consider consistency of the information and agree on the process by the end of September Inform WGMS members of the outcome of this deliberation by the same date allowing them to consider this for their region Provide any additional contaminant data that is not in the ICES Dbase by the end of September Rob provides template for data transmission by the end of April Rob produces draft design by MIME for discussion Finalise output of the study group by mid January and distribute the outcome to WGMS OSPAR secretariat to provide beers at the successful outcome of the work.	Rob, Claire, Stefan, Maria, Els
4f	To provide new data on background concentrations of alkylated PAHs and dioxins.	All members (mainly Céline Tixier, Craig Robinson, Ingemar Cato and Lucia Viñas)
5g	WGMS members are to bring information on the topics identified for the development of a guideline/review on the use of passive sampling for measurements in sediments and approaches to the estimation of pore water concentrations at the next meeting.	All members
5g	WGMS Chairs will contact Kees Booij to become involved in the preparation of the guideline	Chairs
5g, 6k	WGMS chairs will actively search collaboration with WGBC and MCWG on the topics identified during the meeting	Chairs
5i	WGMS members are encouraged to bring new information related to the use of passive samplers in environmental monitoring, particularly related to sediment.	All members

Annex 6: Background paper on concentrations of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) in post-glacial clays of the Baltic Sea

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Abstract: Background concentrations of PCDD/Fs have been studied in two sediment cores from the Gulf of Bothnia and one core from the SW Baltic Sea. The cores were sub-sampled in the oldest part of the postglacial strata at depth varying from 330 to 600 cm. Very low concentrations were found in these preindustrial fine-grained sediments, however, with a clear dominance of furans, indicating forest fires as the most probable sources. The WHO-TEQ2005 in fine-grained sediments seem to vary between 0.23 and 1.5 pg/g dw with a mean of 0.66 ± 0.73 and a median of 0.24 pg/g dw.

Keywords: polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), sediment, background concentration, Baltic Sea.

1. Introduction

There are good reasons for believing that polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) has a natural background concentration in nature, especially given the fact that among others forest fires have always occurred. The magnitude of natural concentrations in preindustrial sediments is more or less unknown, as data in the literature is lacking (see, e.g. Verta *et al.* 2007, Wiberg *et al.* 2009).

There exist a few number of time-trend studies of PCDD/Fs in marine sediments, e.g. Assefa *et al.* (2011), but none of these studies goes as far back in time to get results representative of the natural background. Instead, the reporting has been focused on the post-industrial to recent trends in relation to emission sources (e.g. Wiberg *et al.* 2010). In 2006, the Swedish EPA initiated a project aiming at identifying sources that significantly contribute to the current pollution situation of PCDD/Fs and other persistent organic pollutants (POPs) in the Baltic Sea environment. Several field studies were undertaken. The outcome of the project was summarized and related to other Baltic Sea studies in Wiberg *et al.* 2009. Levels and homologue profiles of PCDD/Fs in surface sediments along the Swedish coast of the Baltic Sea were studied (Sundqvist 2009), but no preindustrial samples were analyzed.

In order to try to remedy to this lack of knowledge, the present subproject started within the framework of the BalticPOPs – a Swedish EPA Programme (Wiberg *et al.* 2010, www.balticpops.se). The starting point in the first step has been to try and answer the question if PCDD/Fs may be found in preindustrial sediment and, if so, at what levels. The present paper deals with this first part. At a later stage, the congener patterns will be investigated in order to state if there exists “typical” preindustrial

patterns. The definition of the word “preindustrial” in the present paper is used for the period from hunter society to at least one generation before industrialization beginning.

2. Methods

Sampling

Selection of sampling sites: The primary criterion for selecting suitable stations has been to core in places where the strata of postglacial clay is thick enough and is covering glacial clay deposited during the recession of the Weichselian land ice (last ice age). With this information, it is ensured that the lowest part of the postglacial clay was formed under preindustrial time shortly after the recession of the inland ice started. Another primary criterion has been to use areas with an undisturbed, continuous deposition of fine-grained sediments.

Hydro-acoustic measurements: Prior to sampling, the sites were investigated with hydro-acoustic techniques such as side-scan sonar (chirp) or in 2011 multibeam echosounder, shallow seismic, sub-bottom profiler and conventional echo-sounder (35/200 kHz). Based on the interpretation of the hydro-acoustic records obtained from each place, the most promising sites were selected for coring (Figure 1).

Sampling: The hydro-acoustics and sampling was carried out from the survey vessel S/V Ocean Surveyor belonging to the Geological Survey of Sweden (SGU). To keep the site position with accuracy better than one metre, the vessel is equipped with a dynamic positioning (DP) system, which means that vibro-hammer-coring was done without anchoring the vessel. Station name, water depth and position data of the sampling sites are presented in Table 1.

Prior to the detailed core description and photo documentation, the cores were subsampled and the samples, put in glass-jars, were immediately stored in a freezer (-20°C) onboard the vessel.

Table 1. Metadata of the core-samples used in the present study.

Core no.	Core length (cm)	Sub sample core depth (cm)	Type of sediment	LOI (%)	Latitude N WGS84 (m)	Longitude E WGS84 (m)	Waterdepth (m)
11_0258	600	520-530	Postglacial gyttja clay	2,6	63 15 58.1	18 43 31.6	15.9
11_0419	600	540-550	Postglacial clay gyttja	2,1	62 28 17.8	17 20 23.2	18.0
01d-0014	430	300-305	Postglacial clay	6,2	55 13 47.5	13 40 04.0	42.4

Chemical analysis

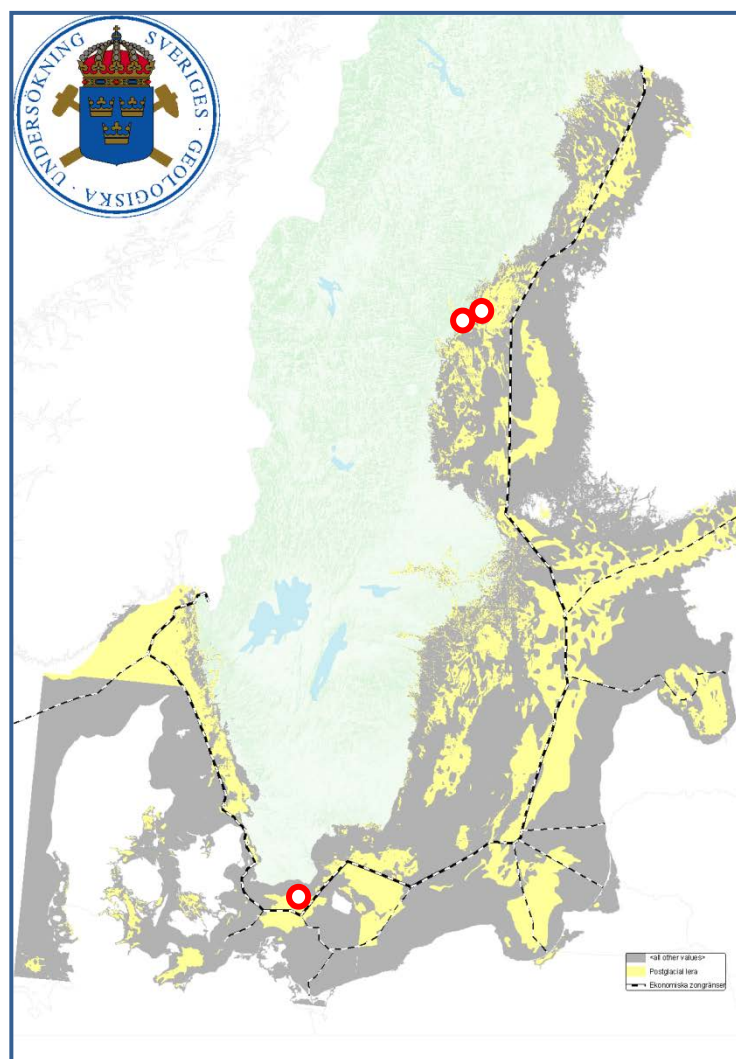
The used chemical quantification methods are well validated by a number of international inter-calibrations. GC-MS analyzes were performed according to Swedish standard SS-EN 1948:1-3. A summary of the analytical methods are listed below.

Sample Preparation: Prior to extraction, ¹³C-labelled internal standards were added. Samples were then extracted with organic solvents.

Purification: The purification of the samples was carried out according to the procedure described in Sundqvist *et al.* 2009.

Analysis: Congener-specific analysis was conducted by gas chromatography – mass spectrometry (GC-MS) and so called isotope dilution technique. A high resolution mass spectrometer (VG 70-250/Autospec) was used. It operated in electron impact ionization (EI) mode and selective ions were recorded (SIR).

Quantification: The MS detection enables to selectively detect substances with specific masses, which means that ^{13}C -labelled internal standards (IS) can be distinguished from native (^{12}C) dioxins. The quantification was carried out under the above mentioned SS-EN standard. Hereby, the ratio between natural congeners and ^{13}C -labelled IS in the sample extract is compared with the corresponding ratio in a quantifying standard containing known amounts of natural and ^{13}C -IS. This procedure results in that the calculated concentrations are compensated for the reprocessing losses.



○ = Vibro-hammer coring site

Figure 1. Sea-bed sediment map of the Baltic Sea, Kattegat and Skagerrak showing areas of post-glacial clay including areas of recent accumulation of fines ($<63\ \mu\text{m}$) in yellow and all other sediment types and bedrock outcrops in grey. Red circles show vibro-hammer coring sites for background studies of PCDD/F.

Calculation of TCDD equivalents (TEQ)

Based on the toxicity equivalence factors (TEFs) and measured concentrations of individual congeners, the TCDD equivalents (TEQ) were calculated. TCDD equivalents relate the toxic congeners to the most toxic congener, 2,3,7,8-TeCDD. $\text{TEQ} = \text{concentration} \times \text{TEF}$. There are several different TEF scales that have been used through the years. Today, the WHO-TEF scale is the most established, but the results can be converted using the scale as desired (Table 2).

Table 2. Scales for the calculation of toxic equivalents (TEQ).

Congene		TEF			
		WHO ₁₉₉₈	WHO ₂₀₀₅	International	Nordic
2378	-TeCDD	1	1	1	1
12378	-PeCDD	1	1	0.5	0.5
123478	-HxCDD	0.1	0.1	0.1	0.1
123678	-HxCDD	0.1	0.1	0.1	0.1
123789	-HxCDD	0.1	0.1	0.1	0.1
1234678	-HpCDD	0.01	0.001	0.01	0.01
	OCDD	0.0001	0.0003	0.001	0.001
2378	-TeCDF	0.1	0.1	0.1	0.1
12378	-PeCDF	0.05	0.03	0.05	0.01
23478	-PeCDF	0.5	0.3	0.5	0.5
123478	-HxCDF	0.1	0.1	0.1	0.1
123678	-HxCDF	0.1	0.1	0.1	0.1
123789	-HxCDF	0.1	0.1	0.1	0.1
234678	-HxCDF	0.1	0.1	0.1	0.1
1234678	-HpCDF	0.01	0.01	0.01	0.01
1234789	-HpCDF	0.01	0.01	0.01	0.01
	OCDF	0.0001	0.0003	0.001	0.001

When a congener not could be detected, the detection limit was calculated. The limit corresponds to a signal from the analyzer, which is three times higher than noise levels. The detection limit will depend on a number of factors and varies slightly from sample to sample, between the various congeners, and from one instrumental run to another.

TEQ was calculated at three levels. A lower concentration limit, in which the concentrations of non-detected substances are set to zero, an upper concentration limit, in which the concentrations of undetected substances are replaced with the detection limit, and a mean concentration (mean of the two). The percentage contribution of detected congeners to the total TEQ value was calculated from the upper concentration limit. The laboratory blank-concentration is reported separately, and no subtraction has been made from the samples' concentrations.

3. Results

The results of the analyses of the pre-historic sediment subsamples are presented in Table 3 together with the laboratory blank. WHO-TEQ₂₀₀₅ values are given for all samples.

Table 3. Background concentrations of PCDD/Fs (pg/g dw) in preindustrial sediment samples from the Baltic Sea.

Sample: Sediment:	No. Depth (cm)	11_0258 (520-530)	11_0419 (540-550)	01d_0014 (300-305)	Laboratory blank
Congene	Year Conc.	2011 pg/g dw	2011 pg/g dw	1995 pg/g dw	pg/g dw
2378 TeCDD		<0,055	<0,011	<0,011	<0,011
12378 PeCDD		<0,037	0,12	0,71	0,058
123478 HxCDD		<0,16	<0,15	0,83	<u>0,15</u>
123678 HxCDD		<0,14	<0,14	1,1	<0,16
123789 HxCDD ^a		<0,027	<0,025	2,89	<0,031
1234678 HpCDD		<u>0,29</u>	0,38	22	<u>0,13</u>
OCDD		0,88	1,5	275	<u>0,29</u>
2378 TeCDF ^b		0,42	0,17	0,15	<u>0,043</u>
12378 PeCDF		0,22	0,095	0,077	<u>0,039</u>
23478 PeCDF ^c		0,11	<0,037	0,037	<0,011
123478 HxCDF ^d		0,21	0,16	<u>0,062</u>	<u>0,032</u>
123678 HxCDF ^e		0,095	0,11	<u>0,051</u>	<0,031
234678 HxCDF ^f		<u>0,099</u>	<u>0,091</u>	0,11	<u>0,069</u>
123789 HxCDF ^g		<u>0,062</u>	<u>0,12</u>	<u>0,13</u>	<u>0,12</u>
1234678 HpCDF		0,15	0,33	0,12	<u>0,043</u>
1234789 HpCDF		<u>0,072</u>	<u>0,068</u>	<u>0,041</u>	<u>0,051</u>
OCDF		<u>0,17</u>	1,04	0,83	<u>0,077</u>
Sum	upper conc.	0,16	0,21	1,5	0,11
WHO-TEQ₂₀₀₅	aver. conc.	0,24	0,23	1,5	0,12
(pg/g dw)	lower conc.	0,33	0,26	1,5	0,14
Bold data = Concentrations < 10 times blank value					
<u>Underlined italic</u> = Concentrations < 3 gånger detection limit					

Concentrations of less than 10 times the blank value and concentrations lower than 3 times the limit of detection are also shown in Table 3. The results show very low levels, in particular for the two preindustrial samples (11_0258 and 11_0419 from sediment depth varying between 520-550 cm) in the Bothnian Sea where the WHO-TEQ₂₀₀₅ were 0.23 and 0.24 pg TEQ /g dw, respectively. In the south-eastern Baltic Sea, the corresponding value was 1.5 pg/g dw (sediment depth 300–305 cm; core 01d_0014). In all three cores, the congener 1234678-HpCDD was detected, together with all of the dibenzo-furans, with only one exception. The dominance of furans may indicate forest fires as the most probably sources.

For comparison, two examples of PCDD/Fs concentrations in recent superficial sediments from SW Baltic Sea (SE-11, HELCOM area) and Skagerrak (Bvvf-Koster-16, OSPAR area) are given in Table 4. The WHO-TEQ₂₀₀₅ values are 6 and 18 times higher, respectively, than the background values found.

Notable is that the WHO-TEQ₂₀₀₅ in core SE-11 taken in the northern Bornholm basin at 0–3 cm and 6–9 cm sediment depth, was 18 and 28 pg/g dw. At 45–58 cm depth (age dating is missing), the WHO-TEQ₂₀₀₅ had dropped to 1.0, i.e. corresponding to above given background concentrations found at far greater sediment depths.

Table 4. Examples of PCDD/Fs concentrations in recent superficial sediment from the Skagerrak Sea (OSPAR area) and the Baltic Sea (HELCOM area).

Station No.:	Bvvf 16	SE-11
Recent sediment:	Open Sea	Open Sea
Sediment depth (cm):	0-2	0-3
Year:	1995	2010
Congene	OSPAR Area	HELCOM Area
Concentration:	pg/g dw	pg/g dw
2378-TCDD	0,4	0,83
12378 PeCDD	0,9	2,4
123478 HxCDD	1,2	2,6
123678 HxCDD	2,1	4,9
123789 HxCDD	2,6	8,5
1234678 HpCDD	30	47
OCDD	186	190
2378 TCDF	3,8	17
12378/12348PeCDF	3,8	>8
23478 PeCDF	3,2	12
123478/123479HxCDF	7,2	>31
123678HxCDF	3,3	12
234678HxCDF	3,7	12
123789HxCDF	0,5	3,6
1234678 HpCDF	18	70
1234789HpCDF	3	6,2
OCDF	74	120
WHO-TEQ ₂₀₀₅	6,0	17,6

Our results from the three sediment cores, which were sampled at these greater sediment depth in the post-glacial clay corresponding to preindustrial times, indicate that the natural background of PCDD/Fs is approx. 1 pg TEQ /g dw (1 ppt). The mean (\pm standard deviation) was 0.66 ± 0.73 and the median was 0.24 pg/g dw (Table 5).

Table 5. Average and median of background PCDD/Fs concentrations in sediment.

WHO-TEQ ₂₀₀₅ n = 3	pg/g dw
Average	0,66
Standard deviation	0,73
Median	0,24
Minimum	0,23
Maximum	1,5

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To PhD Per Liljelind, Head of the Laboratory of Environmental Chemistry, Department of Chemistry, Umeå University, we tender our sincere thanks for a nice co-operation. This study was carried out within the framework of the research programme BalticPOPs funded by the Swedish Environmental Protection Agency (Reg. No. 09/181).

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Annex 7: Technical minutes by RGMON 2012

Reviewers: Jose Fumega and Paul Keizer

Guidance on the design of a regional monitoring programme for contaminants in sediments

This report provides technical comments on the draft advice from the 2012 report of the Working Group on Marine Sediments in Relation to Pollution (WGMS) on the request from OSPAR to provide advice on the spatial design of a regional monitoring programme for contaminants in sediments. Specifically:

“to develop guidance on the design of a regional monitoring programme for contaminants in sediments which can explain whether good environmental status has been achieved on a larger regional scale (e.g. sub-Regions of the OSPAR Regions) within the period 2010–2020, with the major effort in 2014–2020. The guidance should address:

- a. the selection of areas where monitoring makes most sense, i.a.
 - (i) depths that are sensible to monitor (does it make sense to monitor below 1000 m? 500 m? 200 m? 100 m?)
 - (ii) sediment types that are sensible to use and the implication for possible spatial coverage
 - (iii) ship time considerations;
 - (iv) time from changes in inputs to response in the sediment can be detected
- b. the required spatial resolution of sampling within these areas

The guidance should be divided into coastal and open water (i.e. beyond 12 nautical mile limit) and take into account the need to distinguish between point source monitoring and diffuse sources”

In 2011 RGMON2 reviewed material from the WGMS 2011 report that was very preliminary in nature, the intention being to provide the requested advice to OSPAR in June of 2012. The comments of RGMON2 were therefore focused on the general content of the WGMS 2011 report rather than the detailed content. The review of the material provided by WGMS in its 2012 report focuses on the response of the WG to the comments provided by ADGMON2 in 2011.

RGMON comments

The response from WGMS suggests that the request from OSPAR has perhaps been unofficially modified or expanded. The OSPAR request is for advice on sampling design for the purpose of interregional comparisons as per the requirement of the MSFD. However another aspect of the MSFD is that where GES has not been met that member states must show that they are making progress toward achieving GES, i.e. an appropriate temporal trend. According to the WGMS text a decision has already been made that the spatial comparison and the test of whether or not GES is made will be based on the analysis of whole sediments. We presume that there is no reason to argue this point further even if it severely compromises the ability to detect interregional differences or to reasonably assess whether or not GES is met.

WGMS is however continuing to make the argument that it is futile to try to determine temporal trends in sediment contamination by analysing whole sediments. As we understand the WGMS text a pilot study is being undertaken in the southern North Sea to determine the practicality of identifying strata based on sediment type and sediment dynamics. It is not clear what properties of sediment dynamics will be used, perhaps some measure of shear strength to express sediment mobility? Presumably the purpose of this exercise is to provide member states and OSPAR with a stronger basis for arguing the need to explicitly sample fine sediments or else sieve sediments to obtain the fine grain component for analyses.

Given that the information contained in the WGMS report will have already been informally communicated to OSPAR the ADGMON will have to consider what information needs to be formally communicated. The text from the WGMS report lacks clarity and will need to be amended if it will be the basis for the ICES response. We have provided numerous comments in the WGMS text that hopefully assist with the editing.