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Aberdeen, UK

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Contents

Executive summary

The Working Group on Marine Sediments in Relation to Pollution (WGMS) met from 7 to 11 March in Aberdeen, UK. The meeting was chaired by Patrick Roose and Lucia Viñas and attended by 12 scientists from nine 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.

From the onset it was clear that agenda item 3, the spatial design of a regional monitoring programme for contaminants in sediments below was a major task, and, that it would seriously impact the meeting. WGMS realised from the onset that it would be unlikely to deal with this agenda item conclusively at the meeting but that the groundwork could be done with the aim to prepare a draft version by next meeting. Given its importance, it got priority at the expense of the other items on the agenda.

WGMS recognised that contaminants predominantly associate with fine-grained sediment particles, and that the design of a monitoring programme should be based on this property. Although the GES target is not yet defined, WGMS considered that this will in all likelihood be based on total sediment concentration. Nevertheless, WGMS recommends that the importance of grain size distribution be taken into account for the development of EAC and/or GES descriptors and is willing to collaborate on this with WGBEC. WGMS further considered that for the purposes of assessing GES it is unwarranted to conduct extensive monitoring in areas of coarse sediment. Also, suggestions for the number of strata, the number of samples in a stratum, division of the OSPAR area into strata and the frequency of monitoring were considered. WGMS will revisit this agenda item at next year's meeting with the aim to produce a draft version of the guidelines.

Dr Rob Fryer from the host institute was able to input his considerable expertise and experience of developing such sampling designs in helping the group to respond to this agenda item. As the task could not be completed this year, WGMS recommends that a suitably experienced statistician should join the group for this agenda item.

WGMS further investigated the necessity to regionalise pivot values and concluded that there are regional differences between pivot point values. This warrants the development of such whereby the area these pivot values apply to and the repeatability should be considered. WGMS should be requested to define the terms for the development of these values. In the mean time, the existing OSPAR pivot values can be used.

Due to time restraints, work on the uncertainty in data assessments arising from the selection of co-factors could not be fully explored but seems warranted, based on recent results. WGMS should continue to investigate this.

The preliminary background concentrations (BCs) for alkylated PAHs could again not be re-evaluated due to lack of data, but new data should be forthcoming by next year's meeting. WGMS suggest that the proposed BCs are used such as they are, pending a new evaluation.

Finally, results presented on the use of Passive Samplers (PS) confirm the great potential in producing meaningful data on the status of the environment, particularly if GES is envisaged. WGMS will continue work on this topic and aims at reviewing the

use of PS for measurements in sediments and approaches to the estimation of pore water concentrations.

1 Opening of the meeting

The 30th meeting of the Working Group on Marine Sediments in relation to Pollution was opened by Professor Colin Moffat, Marine Assessment Team Leader, Marine Scotland Science, Aberdeen. After a very informative presentation on Marine Scotland, 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. From the onset 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

Shortly prior to the meeting, WGMS was asked 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. subregions of the OSPAR Regions)". Further considerations were that it should include the selection of areas where monitoring makes most sense, specified as:

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

v) the required spatial resolution of sampling within these areas

Furthermore, this 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. (OSPAR request 2011/2).

WGMS realised from the onset that it would be unlikely to deal with this agenda item conclusively at the meeting but that the groundwork could be done with the aim to prepare a draft version by next meeting. WGMS were fortunate that Dr Rob Fryer from the host institute was able to input his considerable expertise and experience of developing such sampling designs in helping the group to respond to this agenda item. As the task could not be completed this year, it is recommended that a suitably experienced statistician should join the group for this agenda item when it is revisited next year.

The task itself raised a number of questions and caused considerable discussion within the group, as is summarised here:

1) What is the scale?

OSPAR document MIME(2) 10/3/Info.1-E on the design of CEMP monitoring noted that "the division of the OSPAR maritime area into the five OSPAR Regions results in areas which are large and heterogeneous, and not at an appropriate scale for representative or meaningful regional assessment" and that therefore "CEMP Monitoring should be designed to enable regional characterisation of a set of subregions, within each OSPAR Region", and that "the main sub-division is between the open sea and coastal waters (within the 12 nautical mile from the territorial baselines)." WGMS agrees with this description. Also, the current subdivision of the OSPAR region as proposed by OSPAR-MIME was presented to the group and no major arguments were raised against it.

Within the time available to WGMS, it was only possible to present guidance for open water monitoring (outside the 12 nautical mile limit), where the OSPAR subregional scale is sensible for assessing environmental status. Guidance on programme design for inshore monitoring should be considered at a future date.

Since contaminants predominantly associate with fine-grained sediment particles, the first step in designing a sediment monitoring programme should be to identify areas where fine grained sediments are present and to use that knowledge to inform the design of a sampling programme. An example of this, based on the Swedish sediment monitoring programme, was documented for the Baltic by Ingmar Cato and Kirsten Jörgensen (Annex 6). WGMS therefore recommends that sampling is stratified, using strata (within subregions) that are primarily defined by sediment type. Stratification should also consider knowledge about e.g. transport of suspended particulate matter, and depth and referring to guidance given in the ICES cooperative report on sediment dynamics.

2) What is GES?

The GES target is not yet defined. It is also not the task of WGMS to come up with a GES target for sediments. However, OSPAR ecotoxicological assessment criteria (EACs) are likely to be used as they are intended to inform upon concentrations above which adverse toxicological effects are likely. WGMS understand that EACs are based upon toxicological information derived from whole sediment chemical testing and that sediment physico-chemical characteristics were not used to inform the process of setting EACs. For example, WGMS believes that toxicological data based on silty sediment may not be appropriate for use in areas of coarse sediment without a method of adjusting for sediment characteristics; however, target values for total sediment are all that are likely to be available in the time scale. The design concepts below would be different if considering concentrations in fines (or normalized concentrations). WGMS recommends that the importance of grain size distribution be taken into account for the development of EAC and/or GES descriptors and is willing to collaborate on this with WGBEC.

3) Should the design address solely assessment against GES, or also include assessments against background and trend monitoring?

In order to maximise the efficient use of ship time, analytical time and the collected information, WGMS felt that the programme should attempt to address the three issues concurrently. However, it is recognised that this will inevitably lead to some compromises and that one objective will need to take priority.

4) Should we only look at silty areas, or should we also include sandy areas?

For the purposes of this discussion "coarse" sediment was defined as containing <2% silt/clay particles (to be confirmed after evaluation of the different areas). Silty sediment was defined as containing >20% silt/clay particles (to be confirmed after evaluation of the different areas).

The group considered that for the purposes of assessing GES it is unwarranted to conduct extensive monitoring in areas of coarse sediment, where concentrations in the total sediment are likely to be low. However, much of Region II (for example) is relatively coarse sediment and therefore, in order to demonstrate GES convincingly on the subregional scale, it is important to have some samples from the areas of coarse sediment and not only in the depositional areas of finer sediment

5) How many strata? How many samples in a stratum?

A risk-based sampling strategy suggests that a low level of sampling is likely to be required in areas known to have low concentrations and/or low variability. A higher intensity of sampling is likely to be required in silty areas, where total sediment concentrations are likely to be higher and more at risk of exceeding the GES target. Some deep sea areas have been shown to have lower variability in concentrations than do shallower, more energetic, areas and so are likely to require a low level of sampling effort.

The subregion should be divided into a small number (up to 5) of strata of relatively homogenous sediment. These strata should include known depositional areas which typically have at least e.g. 20% fines and constitute at least e.g. 2% of the subregion.

Sampling effort in each stratum will then need to be sufficient to demonstrate that concentrations in the strata are below the target value and will depend upon the variability in concentrations within the stratum.

Following discussion, WGMS decided that GES in a stratum would be achieved if the mean concentration in the stratum is below the target value. Other options considered included assessing the proportion of the area with concentrations below the target value; however such options, although possibly more protective, are likely to present operational and statistical difficulties, particularly when trying to make use of existing monitoring networks. WGMS considered that GES targets should be sufficiently protective to allow for the use of mean concentrations in GES assessments.

GES in a subregion would be achieved if the mean concentration in all strata is below the target value. If GES is not achieved, then there is the need to investigate the reasons and to implement management measures (if possible) for those strata where mean concentrations are above the target value.

A sufficient spatial resolution of sampling would be required to ensure that there is low risk of incorrectly concluding that GES has been achieved. How this will be specified will depend on whether GES is assessed by conducting a significance test or by simply comparing the estimate of the mean concentration to the target value.

Monitoring within each stratum can itself be further stratified. For example, by national monitoring regions; a stratum of predominantly sandy sediment could be substratified into mud (the small patches that exist) and sand; a stratum with oil platforms could be substratified into areas within 3 km of a platform and further than 3 km from a platform. But it is important that it is possible to combine the data from the different strata. This is relatively easy to do if the target measure is the mean concentration, but much harder with e.g. percentiles.

The easiest sampling design to work with is simple random sampling or stratified random sampling (to ensure more even coverage). However, there will be pressure to use existing monitoring networks that are often grid based. This might be acceptable if the monitoring network can be thought of (approximately) as a stratified random sample with a large number of strata.

For OSPAR Region II, possible subregional strata might be:

- Northern North Sea: the Fladen Ground (depositional area), East Shetland Basin (despositional area), and the rest (mostly sandy);
- Norwegian trench: single stratum;
- Skaggerak: strata could be Skaggerak (depositional area), Kattegat (depositional area);
- Dogger Bank: single stratum;
- Southern North Sea: single stratum;
- Channel: single stratum.

6) What fraction of the sediment should be analysed?

This caused considerable discussion as it was felt that the answer depended very much upon how the GES target is going to be defined. WGMS recommend that the GES target values should be based not only on total concentrations in sediment, but also on the availability (speciation) of contaminants that mainly depends on the physico-chemical composition of the sediments. However, it seems probable that the GES target value (particularly in the initial assessment) will be based upon on the results of whole-sediment toxicity testing (e.g. existing OSAPR EAC values).

WGMS felt that it should be possible to collect sediments from the same sampling locations in order to address comparison with GES, BACs and for time-trends, but that this needed to be statistically tested using existing datasets.

WGMS felt that where existing time-series exist, these should be continued as they allow comparison with BACs and temporal trends, and that in some cases these time-series may also be suitable for comparison with GES target values. However, datasets based upon the determination of concentrations in the fine fraction may not be suitable for comparison with GES target values based upon data derived from whole sediments.

An option WGMS considered was whether it may be possible to back-calculate concentrations for the total sediment based upon concentrations in the fine fraction and measurements of sediment grain size composition. It may not be possible to do this without introducing an unacceptable level of bias into the assessment, however this needs to be tested on realistic data from different sediment fractions. Current OSPAR advice for assessing data from unsieved sediments against background is to normalise analyte concentrations using co-factor concentrations and the pivot-point procedure (OSPAR CEMP Assessment Manual, 2008). One option (yet to be tested) is whether this normalisation procedure could be used in reverse, in order to compare data from sieved sediments with GES target values based upon data derived from unsieved sediments.

7) How frequently should sediment monitoring be undertaken?

In the targeted depositional areas, the sedimentation rate should be estimated and used to inform upon the frequency of sampling. For example, if the surface 1 cm is sampled, and the sedimentation rate is 1 cm / 5 years, then it is realistic to sample no more than once every 5 years.

If areas of coarse sediment are shown to have low concentrations (below the GES target value) then sampling should be undertaken infrequently in order to demonstrate that the environmental status remains good. The difference between the determined concentrations and the GES target values should be taken into account in deciding sampling frequency e.g. areas that are far below GES will require less frequent monitoring.

It should be noted that fine-grained sediment particles (and the contaminants associated with them) are moved around regions depending upon the hydrodynamics. Thus, in order to be able to inform on measures to take if GES is not achieved, an understanding of sediment dynamics is required in order to identify the potential source(s) of contaminants. However, sediments are informative of chronic contaminant inputs and remedial measures may take very long time periods to produce a response. In this case, analysis of the fine fraction in coarser sediments can be informative of the success of remedial measures more quickly than by only monitoring the depositional areas that may be remote from the source of contamination.

WGMS will revisit this agenda item at next year's meeting. Intersessionally, WGMS members will take steps (see actions) to ensure that a draft version can be produced during that meeting.

4 Review and comment on the report of the 2010 meeting of OSPAR/MON in relation to sediments

WGMS did not go through the assessments made by OSPAR MIME (formerly MON) due to the priority given to agenda item 3 above and the fact that it was felt there was not a major need to give input into the ongoing assessments. The division of the OSPAR area into subregions was presented to group as an input into the discussions during agenda item 3. Furthermore, various aspects of the assessment process were part of the discussions concerning agenda item 3, 5 and 4. Patrick Roose also gave a short presentation on the OSPAR QSR 2010 and introduced the QSR website to the group.

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

Pivot values represent the concentrations of contaminants and cofactors in sediment containing no fine-grained material, i.e. in sand. In 2009, WGMS expressed the main concern regarding pivot values was that the composition of sand-sized material may differ significantly between different parts of the Convention area. The use of inappropriate pivot values could have significant impact on the calculated normalised concentrations, particularly for sediment samples containing relatively small proportions of fine-grained material. Most pivot point values are zero for organic contaminants, so tests have only been completed on trace metal pivot point values.

Last year, members present at WGMS2010 reviewed limited information available and compared with the current pivot values with their uncertainties. As agreed in WGMS 2010, many members, including representatives from UK, Spain, and France submitted further concentrations of contaminants and cofactors in sediment containing no fine-grained material ideally, i.e. in sand. Concentrations were also accepted from sediments with less than 5% silt/clay (<63µm) or less than 2% clay (<20µm) with the realization this would be a possible source of variability (rather than regional differences). This data was then put into OSPAR regions, as for the previous limited test completed in WGMS2009, because the WGMS advised that regionalised pivot values should be applicable over large parts of the Convention area, for example across entire Regions, or to all monitoring data from a particular country.

One observation is the large natural variability in concentrations for sand on a regional scale, and data collected supports this. For concentrations measured in Region II and Region III, most of the values are within the grey band. For Region IV, some of the median concentrations are outside the grey bands. There are several reasons, other than regional variation that this may be occurring. Several samples are measured on <2mm fraction with a small amount of the fine fraction, so there may be some input from this small amount of fine fraction.

Where there is high variability of pivot point values in the OSPAR regions the values should be investigated on a subregional basis. It would then be possible to determine whether this variability was because different regional boundaries existed than the OSPAR regions.

It is clear there are regional differences between pivot point values from data provided this year and therefore the following is recommended: CPs are invited to submit pivot point values for use in OSPAR trend assessments, to WGMS for approval, alongside supporting evidence showing the validity of such data. It should be clear what area these pivot values apply to. Also, there should be sufficient spatial coverage for this area, and sufficient repeatability. WGMS should be requested to define what is sufficient by referring to the original dataset used to produce the OSPAR pivot values (OSPAR, 2008) next year. If no values are submitted for a Region the default will be to use the existing OSPAR pivot values.

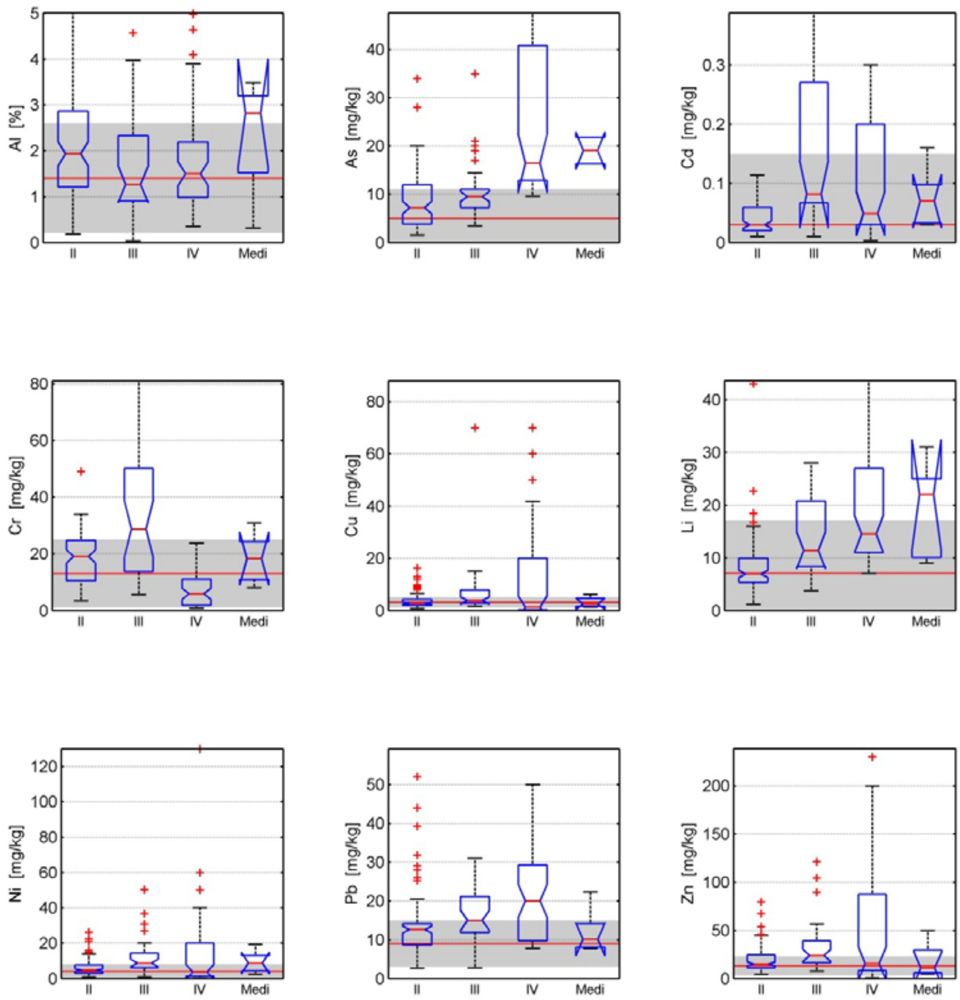

Figure 5.1. Box plots showing pivot point variability for each OSPAR Region. The pivot value used for OSPAR normalisation is given by the red line and the grey bands show the natural variability in pivot values used to calculate uncertainty in the OSPAR normalised values (2 X standard deviation (sNx) as given in CEMP manual (OSPAR, 2008)).

6 To continue work on the uncertainty in data assessments arising from the selection of co-factors.

This agenda item originates from 2009 were WGMS invited CPs to present proposals for the specification of co-factors to be used for the normalisation of concentration of particular contaminants in their monitoring data. The effectiveness of the normalisation would be assessed through its effect on reducing the residual variance about the time series. WGMS 2010 was asked to report on how the uncertainty associated with the use of co-factors may impact on data assessments. During that meeting, a limited dataset consisting of German and French data was evaluated by a subgroup demonstrating that there were good linear relationships for most elements for clean stations and, that trace metals data from the <20 µm fraction does not require normalisation. Further work was required on this, with a larger dataset and this was planned for the 2011 meeting. WGMS2010 requested that additional data be obtained to further this work and recommended that a statistician with expertise in assessment procedures would examine how the use or none-use of differing co-factors affects the assessments. The effectiveness of the normalisation would be assessed through the effect of application of normalisation on the residual variance about time series, as described in WGMS2009. In the absence of accepted new proposals, the existing approach should continue to be used.

At the 2011 meeting it was recognised that, due to the impact of agenda item 3, there was not sufficient time to work on this at the meeting. The group decided to focus on whether regional normalisation pivot points are required (agenda item 5) and also assumed that this aspect would resurface during the development of agenda item 3. The item will have to be discussed again at next year's meeting, particularly in relation to TOC that has not been investigated at all.

Claire Mason presented results from a study completed in the UK which aims to derive regional baselines for use of assessment of trace metal concentrations at dredge disposal sites, using the principals of normalization as advocated by the WGMS in 2009. Trace metal concentrations are measured on the fine fraction (<63μm) using a total HF digest to assess extent of impact of dredge disposal at dredge disposal site surveyed in England and Wales. When these concentrations are compared to OSPAR Background Assessment Concentrations, they are frequently above these across the whole survey area (from sites within and outside the disposal site). The English and Welsh coastline is well known for having widely variable geological differences and it is likely for the purposes of localised disposal site assessments, regional baselines are required. Trace metal concentrations from a wide range of projects were collated, including two large spatial grids, for England and Wales, as well as dredge disposal survey data. The data was subdivided into eight regions, as for the CSEMP Redesign programme, a pilot study set up to trial spatial regional monitoring. These are based on bio-geographic regions identified defined principally by reference to physical and biological features such as tidal fronts and seabed flora and fauna.

There is a clear need to normalise metal concentrations as these regions contain a mixed range of sediment types. Most of the trace metal concentrations are measured on the fine fraction (<63μm) and so therefore normalisation is already completed. However, in the OSPAR guidance, further geochemical normalisation is advised as useful, even on the concentrations measured on the fine fraction (<63μm). Therefore the normalisation method defined in the OSPAR guidance was used to produce normalised values for five different cofactors, Al, Li, Rb, organic carbon and clay content, for each region. Different baseline approaches, including the OSPAR BAC method (OSPAR, 2008), and frequency distribution method (Rodriguez *et al.*, 2006) were also tested.

Relationships between cofactors and each trace metal were tested using correlations, and it was clear in this combined dataset while there were good relationships between individual metals, the relationships between cofactors and metals were not strong. Li performed the best overall, but for some regions Al was better. However, none of the relationships between trace metals and cofactors tested were strong enough to reasonably use for further normalisation on the fine fraction ($r < 0.8$). It is clear that if relationships between trace metal concentrations and cofactors are not checked, then spurious values can result.

When baselines calculated with normalised values to the cofactor that are best correlated with trace metal concentrations are compared with baselines calculated with raw data (<63μm) then similar baseline results are achieved. Therefore for these regions and with sediment data measured on the fine fraction (<63μm) where the relationship with co-factors is not strong, further geochemical normalisation with cofactors is not required.

This work will shortly be submitted for publication (Mason, C., Bolam, T., Barry, J. and Smedes, F., in prep., Determination of regional baselines of trace metal concentrations for disposal site assessment in England and Wales).

References:

Rodriguez, J.G., Tueros, I., Borja, A., Belzunce, M.J., Franco, J., Solaun, O., Valencia, V., and Zuazo, A., 2006, Maximum likelihood mixture estimation to determine metal background values in estuarine and coastal sediments within the European Water Framework Directive, Science of the Total Environment, 370, 278-293

OSPAR Commission, 2008: Co-ordinated Environmental Monitoring Programme – Assessment manual for contaminants in sediment and biota, OSPAR, 39pp

7 Continue collection of data and develop background concentrations for alkylated PAHs.

Due to the lack of data, this work could not be undertaken at this meeting. WGMS fully recognises the need to continue this work and members were again asked to provide data on

8 Passive sampling

8.1 Provide a document discussing the different passive samplers presently used

Although such a document would indeed be very interesting and potentially useful, it was mentioned at the meeting that a number of recent scientific reviews and book chapter on passive sampling is available. Some of these publications review many of the devices available nowadays for passive sampling measurements in water and sediments. A review of passive sampling measurements in sediments and approaches to the estimation of pore water concentrations is currently missing. Much work recently has focussed on the measurement of contaminant concentrations both in the laboratory and *in situ*.

Brief discussions in Aberdeen included the preparation of a list of passive sampling devices that may be used for a range of measurements of bioavailable contaminants in sediments. Since samplers can be used in many different ways, it may be possible to provide a description and some general guidelines for the adequate implementation of these tools for various measurements. Recent applications include exposures in batch laboratory experiments to for the measurements of pore water concentrations or the measurement of the entire bioaccessible fraction using an infinite sink approach. Attention has been drawn to the possibility of measuring diffusive fluxes and concentration gradients between overlying and pore waters. Since passive sampling devices measure dissolved concentrations, a question was raised regarding the use of passive sampling data for compliance checking against environmental quality standards (based on total concentrations, for water or sediment phases). Attention was brought to the importance of black carbon and other amorphous organic matter phases in the often high apparent sediment-pore water partitioning observed in sediments.

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

As identified at the WGMS workshop in 2010, the possible use of passive samplers as a proxy for partitioning to sediment was also briefly discussed. Since very little time was allocated to this task, no further discussions have taken place. However, we fully recognise the need to pursue this work in the future.

8.3 Report ongoing and new projects involving passive sampling

Patrick Roose gave an update on latest developments of the INRAM project. The project has been running for 4 years and in the original scheme and the final report was due in January of 2011. However, the Science Policy office granted an extension to the programme of 6 months and the new deadline for final reporting is June 2011. The final report will therefore be available at next year's meeting. The project focussed on integrated monitoring of contaminants in the Belgian coastal zone and major harbours. For the purpose of this meeting, only work related to passive sampling was presented. In the project, passive samplers were used both to determine time-integrated concentrations of chemicals and to perform ecotoxicity tests. In the latter, test organisms were exposed to samplers collected in the field. A clear and significant effect could be observed when the organisms were exposed to samplers, for instance, from the harbour of Oostende. In recent developments, the project investigates the applicability of passive samplers as a reference phase linking the different compartments (sediment, water, biota) with the effects of contaminants through equilibrium modelling. There was a clear interest for this approach and it can be expected that more information related to this topic will appear the next years. The final results of INRAM will be presented at next year's meeting.

Céline Tixier gave a short presentation on an laboratory intercomparison exercise on passive samplers, which took place in France in 2010. This exercise was organised in the frame of the AQUAREF program (a consortium of five French institutes involved in water monitoring http://www.aquaref.fr). Participants were expert laboratories involved in passive sampler development and deployment from France and Europe. The main goal was to assess the potential role and efficiency of passive samplers for the measurement of pollutants in surface water and coastal water. Three sampling campaigns were organised between April and July 2010 for the measurement of metals, polycyclic aromatic hydrocarbons (PAHs) and pesticides in both continental and marine surface waters. Trials were conducted on two rivers and on one marine site (Thau Lagoon, France). The passive samplers used included POCIS (Polar Organic Chemical Integrative Sampler), SPMD (Semi-Permeable membrane Device), membranes (LDPE, silicone), Chemcatcher, MESCO (Membrane-Enclosed Sorptive Coating) for organic contaminants; and DGT (Diffusive Gradient in Thin Film) and Chemcatcher for metals. A total of 24 laboratories took part in this exercise, among them several members of WGMS. To enable the comparison of integrated with spot sampling, reference laboratories were in charge of chemical analysis of spot surface water samples collected at regular intervals during the campaigns. Moreover, to enable a thorough interpretation of passive sampling results, flow velocity, temperature and several physico-chemical parameters in surface waters were determined at each studied site. Data assessment is in progress. Firsts results will be presented at the next International Passive Sampling Workshop and Symposium (IPSW 2011, Krakow, Poland, May 2011) and a final workshop with all participants is planned in the autumn 2011. This *in situ* intercomparison exercise should improve the harmonization of practices for the passive sampling tools, especially for priority chemical monitoring and regulatory programs in compliance with the WFD or MSFD.

The presentation by **Ian Allan** summarised some of the work conducted at NIVA over the last year on passive sampling measurements of organic compounds present in contaminated sediments. Results from batch experiments using low density polyethylene membranes exposed to three contaminated sediments were shown. Pore water concentration measurements and resulting distribution coefficients for PAHs and PCBs for sediments from Oslo and Kristiansand harbours and from a contaminated fjord in the south of Norway (Frierfjord). He also presented data on the static exposure of solid phase micro-extraction fibres (SPME) inserted into sediments to measure PAH and PCB mobility and pore water concentrations. This work demonstrated a clear reduction in contaminant mobility and pore water concentrations upon remediation with 5 % (w/w) activated carbon. Finally he presented data on the use of passive samplers (semipermeable membrane devices; SPMDs) to map and understand the distribution of PCBs along a small watercourse in Oslo (Norway) and the impact of bed sediment contamination on overlying water concentrations.

Kirsten Jørgensen provided a brief presentation of ongoing passive sampling projects in Finland. A research team in Jyväskylä (Heidi Ahkola, Sirpa Herve and Juha Knuutinen) deployed the Chemcatcher (C18) passive sampler for their project " Monitoring of harmful substances in aquatic environment by passive samplers" in the Baltic Sea water in collaboration with the BONUS project BEAST (Biological Effects of Anthropogenic Chemical Stress: Tools for the Assessment of Ecosystem Health). The BEAST project is led by Dr. Kari Lehtonen at SYKE and involves 16 institutes from 9 countries around the Baltic Sea. Passive samplers were deployed outside Kotka in the Gulf of Finland in 2009 and data on biological effects on mussels are also available. Concentrations of a wide range of contaminants will also be measured in mussel tissues. The project used caging experiments, biomarkers and bioindicators in relevant target species (new species from species-deficient areas of the Baltic). Many areas in the Baltic Sea suffer from hypoxia. An attempt to oxygenate bottom waters by circulating water from above the halocline to below by submerged pumps is being tested in two areas in the Swedish and in the Finnish archipelago (PROPPEN-project). The aim is to reduce the load of phosphorous from the bottom sediments to the water column. The impact of this oxygenation may have strong impact on contaminants in the sediment. These impacts are studied in the BASE project– Baltic Sea sediments and changing environmental conditions (part of FIXME consortium) by Jaana Koistinen and Kirsten Jørgensen. In collaboration with the PROPPEN project sediment was sampled from the Sandöfjärden in the archipelago in the Gulf of Finland in 2010. Contaminant and functional degradation genes concentrations in the sediment are analysed before and after the oxygenation in order to study the impact and fate on e.g. PAHs. Furthermore passive samplers were placed in the water column just above the sediment.

Craig Robinson's presentation was entitled "applicability of passive samplers for contaminants monitoring in the UK marine environment". Contaminant monitoring for priority pollutants is an integral part of the UK obligations under the Water Framework Directive (WFD) and OSPAR monitoring programmes. Also, the Marine Strategy Framework Directive (MSFD) requires Good Ecological Status (GES) to be maintained. Descriptor 8 of GES states that concentrations of contaminants are at levels not giving rise to pollution effects. It is therefore important to create a record of baseline contaminant data for current and future needs to establish whether environmental concentrations of chemicals on existing EC and OSPAR chemical priority lists are of toxicological significance (i.e likely to produce pollution effects), and whether there are additional substances with potential to cause harm in the UK marine environment. In order to inform this process, passive samplers were deployed to provide information on presence and freely dissolved concentrations of a wide range of potential target substances for monitoring programmes. The survey covered a wide range of locations around the UK, from industrial estuaries to relatively unimpacted offshore waters. Samplers were deployed for periods of 4–8 weeks during spring and summer 2009. In a smaller subsequent follow-up survey in early 2010, samplers were also deployed alongside mussels. This presentation will include an overview of the project undertaken; the advantages and disadvantages associated with undertaking such a survey using these methods, the establishment of sampling rates for compounds previously unstudied using these methods and some preliminary results from stage 1 survey.

Thi Bolam presented a feasibility study on the application of DGT technology to the monitoring of disposal site cores. Diffusive Gradients in Thin films (DGT) passive sampler is used to determine the "labile" fraction of the chemical species within sediment pore waters and therefore provide a better description of the concentrations of metals and other contaminants exposure to sediment fauna. In the present study, preliminary studies were carried out to test the performance of the DGT methodology and were trialled on the cores taken at the Souter Point disposal, capping and reference sites in 2009 and 2010. Initial sediment profiles show a consistent metal supply for Cd, Cu, Ni and Zn at the water-sediment surface at both disposal and reference cores, which implies that the observation is not related to the disposal activity. The profiles also show differences between core sites. Associated measurements (such as O_2, particle size analysis, carbon determination, chlorophyll, nutrients and porosity) were also analysed in order to better understand the behaviour of metals remobilisation in the sediment. The data are yet to be made available for the interpretation. A DGT study was also combined with SPI (Sediment Profile Imagery) technology to help chemical detection alongside SPI images in the aim to address questions relevant to disposal site management and seabed health. The Apparent Redox Potential Discontinuity Depth (aRPD) delineates the changes between the paler oxidised surfacial sediments and darker reduced sediment at depth. Study carried out by Teal *et al*. (2009)[1] described aRPD as mainly chemically associated between Mn and Fe reduction boundaries. When plotted using the method as described in Teal, Parker *et al.*, close transition between Fe and Mn at two sites in the North Sea (North Dogger and Oyster Ground) related to depth and SPI colour was observed. The strength of the coupling was weakened by heterogeneity at the Oyster Ground due to bioturbation processes. Similar plot was applied to the disposal and reference cores and the plot illustrates that the Fe/Mn transition with depth seems to have broken down at all sites. This is likely to be linked to historical disposal and layering of sediments with contrasting metal loads which disrupts the conventional diagenetic sequence. DGT applications, alongside with SPI technology could be an alternative way of assessing biological exposure to contaminants loads at the disposal sites. However, further investigations are necessary in order to compare the outcomes with the conventional disposal site monitoring sampling method.

[1] Teal, L.R., R. Parker, *et al.* (2009) Simultaneous determination on *in-situ* vertical transitions of colour, pore-water metals, and visualisation of infauna activity in marine sediments. Limol. Oceanol. 54 (5): pp 1801–1810.

Craig Robinson's contribution was entitled "Developing Capacity for Integrated Assessment of Contaminants in Scottish Waters". This programme has been developed to put Scotland in a position to demonstrate and use the OSPAR / ICES approach to the Integrated Monitoring of Contaminants and their Biological Effects. The programme utilises flatfish (dab and flounder) and mussels as sentinel species. The approach involves measuring multiple toxicological endpoints, and determining animal contaminant burdens, sediment contaminant loadings and water contaminant concentrations. Passive sampling of sediments and the water column is included within the scheme. Ten fishing sites have been sampled in each of 2 years and 8 mussel sites have been sampled over two years. Data are still being produced from the fishing sites. An initial evaluation of the first year's mussel sampling (the Clyde) indicated that mussels from the site with highest aqueous freely dissolved PAH and PCB concentrations were also severely stressed when assessed using lysosomal membrane stability of haemocytes. Data will continue to be assessed using the "traffic light" system and different parameters aggregated as the integration scheme is developed. Assessment criteria for concentration data obtained by passive sampling require to be developed and the passive dosing approach may be helpful in this respect.

Emmanuel S. Emelogu presented a field application of passive sampling/dosing techniques in biological effects assessment of hydrophobic organic contaminants (HOCs) from an aqueous environment. Contamination of the aquatic environments with hydrophobic organic contaminants (HOCs) such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and some pesticides is a continuing environmental concern. Monitoring and assessment of biological impacts of HOCs in the aquatic environment is therefore crucial. Nevertheless, the conventional procedures for the assessing impacts of HOCs in aquatic environments are not only challenging but do not generally take account of bioavailability. Further, in aqueous toxicity testing of HOCs, (e.g. exposing live aquatic organisms to test compounds) it is often very difficult to obtain stable exposure conditions due to volatility, adsorption and low solubility. This leads to poorly defined exposures, high variability and potentially erroneous conclusions. Polydimethylsiloxane, (PDMS) silicone rubber can be used to monitor the freely dissolved (bioavailable) concentrations of HOCs (log K_{ow} from ~3 to ~7.5) in aqueous media. In this on-going study, silicone rubber passive sampling technique was applied in determining the freely dissolved concentrations of mixtures of PCBs, PAHs and hydrophobic pesticides from 1 estuary and 4 streams in the River Ythan catchment, NE Scotland. The HOCs extracted from the silicone rubber samplers were spiked into silicone rubber O-rings for passive dosing of *in vitro* toxicity testing systems using rainbow trout gonad (RTG-2) cell line. RTG-2 cell line serves as a suitable alternative to the use of fish in toxicity assessment and offers good mechanism and mode of toxicity effects; the silicone rubber O-rings serve as passive carriers and regulators of stable dissolved concentrations of the contaminants in *in vitro* toxicity assays. Cytotoxicity assays, including endpoints such as neutral red uptake and mitochondrial function (MTT), have been modified and adopted to suit the RTG-2 cell-line and the O-ring passive dosing system. These bioassays with silicone rubber O-rings and RTG-2 cell line will be used to assess the water quality of the Ythan catchment in this study.

Craig Robinson also showed passive sampling-based estimates of freely-dissolved background and background assessment concentrations for PAHs and PCBs in Scottish waters. The use of passive sampling to determine the freely-dissolved concentrations of contaminants in marine environments has been advocated by many authors, and is recommended by Expert Groups of the International Council for the Exploration of the Sea (ICES) and OSPAR Convention, for inclusion in integrated assessments of contaminants and their effects. Silicone rubber (polydimethylsiloxane; PDMS) is increasingly widely used as a reference phase for the determination of polycyclic aromatic hydrocarbons (PAHs), chlorinated biphenyls (CBs) and other hydrophobic organic contaminants. However, little information is available on the background freely-dissolved concentrations of such contaminants. PDMS samplers were deployed for 4 weeks in October 2009 at 6 sites in the NW of Scotland where there are very limited local inputs. Samplers were subsequently Soxhlet extracted and PAH and CB concentrations determined by GC-MS and GC-ECD respectively. Performance Reference Compounds were used to correct for the sampling rates at each site and freely-dissolved concentrations obtained. Background and Background Assessment Concentrations (BCs, BACs) for individual PAH compounds were calculated from these. By OSPAR definition, BCs for PCBs are zero, although low concentrations (LCs) can be derived from concentrations at "remote/pristine" sites. Here, BC/LCs were defined as the median concentrations, and BACs as 3 x the median which is consistent with OSPAR Guidelines. Freely-dissolved total PAH concentrations (Σ38 parent and alkylated compounds) were in the range 6.9-36 ng/l, ΣICES-7 CBs were 35-95 pg/l and total CB concentrations (Σ28 congeners) were in the range 90-215 pg/l. Example BC/LCs and BACs include 1.7 and 5.2 ng/l for naphthalene, 6 and 20 pg/l for benzo[*a*]pyrene, and 16 and 48 pg/l for CB118.

Maria J Belzunce presented the application of a multidisciplinary approach (hydrodynamical, chemical and ecotoxicological) to obtain an integrated evaluation of the environmental quality of the Oiartzun estuary (Biscay Bay, North of Spain). This has been attained by a combination of a hydrodynamical descriptor, with chemical and ecotoxicological results. In this study, a hydrodynamical model was applied to describe the water residence time in the whole estuary. The metal freely dissolved fraction in waters was evaluated by the use of Diffusive Gradient in Thin-Films (DGTs), representing the fraction most potentially bioavailable to biota. Additionally, Toxicity Identification and Evaluation (TIE) procedures were carried out in sediments to identify the chemicals responsible of toxicity. Samples were physically/chemically manipulated to reduce the bioavailability of specific contaminants (metals, organic compounds and ammonia) and toxicity reduction was proven by acute amphipod (whole-sediment; *Corophium sp.*) and sea-urchin bioassays (elutriate; *Paracentrotus lividus*). The results show the highest toxicity in those sediments located in the internal part of the estuary which presents the highest residence time and highest metal concentrations in waters. Contrarily, in the outer part of the estuary, where the average residence time was calculated as the lowest, sediments do not show toxicity to the tested organisms and the metal concentration measured by means of DGTs were lower than in the inner parts. TIE techniques identified organic compounds and ammonia as a mean cause of toxicity in the inner area of the estuary. On basis of results, the application of techniques based on contaminants labile fraction and bioassays results provide a reliable indication of potential effects on the biota. Furthermore, the computed residence time proved to be a coherent descriptor to understand the fate of contaminants in dynamic systems.

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

No questions were submitted to the group.

10 TIMES papers on the analysis of dioxins and PCBs

Patrick Roose informed the group about the evaluation of both papers at MCWG in the week preceding their meeting. The dioxin paper is reaching a final stage and WGMS members were invited to comment on the document as they saw fit. No comments were forwarded by the group.

For the TIMES paper on PCBs, a number of issues were raised during MCWG. This included authorship, the concern that there was too much information on older techniques and not enough on more recent developments, and too much detail in places, particularly on sampling. The lead authors agreed to do a major revision of the paper in the intersessional period and a new version will be made available at MCWG2012 and WGMS2012.

11 Plenary presentations

Apart from the plenary presentations under agenda item 8 above, Ingmar Cato, Marie Russell (Marine Scotland Science) and Maria J Belzunce presented information that was of general interest to the group.

Swedish sediment monitoring programme

Ingmar Cato

The objective of this monitoring program of sediment is to determine the status and/or long-term trends of toxic contamination in both open sea areas throughout the Swedish territorial waters and Exclusive Economic Zone (EEZ). Furthermore, the open sea programme should also be regarded as a complement to similar coastal monitoring programs run by regional authorities as well as local recipient monitoring programs carried out in areas where industries and municipalities are using coastal areas as a recipient for discharging treated waste- and sewage water.

The monitoring programme has mainly been designed in line with the outlined programme agreed upon by the HELCOM MONAS ad hoc Working Group on Sediment Monitoring of the Baltic, the Kattegat and the Belt Seas. In addition to this it is recommended that the monitoring programme also meet the requirement of the MORS-PRO radioactivity monitoring in sediments (HELCOM).

The primary criterion for selecting suitable sites for monitoring, is to find places that are representative of large open sea areas and to avoid local, near coastal contamination close to urban areas. Another criterion is to use areas where there is an undisturbed, continuous and recent deposition of fine-grained (<63 µm) sediments. With undisturbed sediment means no bioturbation, no physical disturbance from waves and bottom currents action, and/or anthropogenic disturbances due to human activities (e.g. trawling, anchoring). Such places are in general found in depressions or basins, often with anoxic bottom conditions.

Sediment cores, taken at each site, are drained, sliced), transferred to plastic jars and stored frozen until later analysis of major and minor elements, organic carbon, nitrogen.

One core from the master site is sliced in 1-cm thick subsamples, from top to bottom, for isotope analyses (e.g.137Cs, 210Pb) aimed at dating and estimation of the accumulation (deposition) rate for the station. The isotope analyses and estimation of the sedimentation rate is carried out once for each station and is not repeated if the station is used for trend monitoring.

For each site, the top-most centimetre (0–1 cm) is taken, pooled, mixed and transferred to a glass jar. These are mixed and homogenized into one large sample representing the entire station, and stored frozen for later analyses of elements, organic carbon, nitrogen and organic contaminants. Due to the cost of analyses, e.g. for meeting the requirements of the WFD-directive, these target substances are only analysed in this pooled-sample to reduce the costs.

The inhomogenity of the sediments within a station is sorted out through the statistical treatment of the seven surface samples by using the major and minor elements and organic carbon. Seven samples are considered to be the minimum number of samples (data) needed to achieve a statistical probability.

The number of cores, subsamples and amount of sediment needed depends on the task and the target that has to be achieved

PBDEs in the Firth of Clyde: A Puzzle

Marie Russell, Lynda Webster & Ines Hussy (Marine Scotland Science)

The Firth of Clyde is a partially enclosed sea loch with current and historic inputs of domestic and industrial wastes (e.g. military bases, engineering works, paper and textile industries, power stations, dredge spoil and sewage (historic) dump sites). As such it is considered to be the most contaminated water body in Scotland. The Clyde Trend Monitoring Program has monitored the concentrations of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in plaice liver and sediment from several sites in the Firth of Clyde since at least 1992 (Garroch Head and Pladda since 1992; Holy Loch, Skelmorlie, Hunterston and Irvine Bay since 1999). Whilst concentrations of PBDEs in plaice liver from Hunterston were similar to the other sites in the Clyde the concentrations in the sediment were not. For all sites bar Hunterston the ICES7 PCB concentrations are higher than those of the PBDEs. At Hunterston the reverse is true. To further investigate the concentrations of PBDEs and PCBs in sediments from the Clyde, cores were collected from Hunterston, Garroch Head, the Holy Loch and a reference site at Kilbrannan Sound (also in the Firth of Clyde) in 2009. Garroch Head is the location of a former sewage sludge dump site and the Holy Loch site is close to a former naval base and a dredge spoil dump site. A nuclear power station is located at Hunterston. Furthermore all sites will be subject to contaminant inputs from sources further up the estuary. PBDE concentrations (sum of nine congeners (ΣPBDE9); BDE28, BDE47, BDE66, BDE100, BDE99, BDE85, BDE154, BDE153 and BDE183) were found to be significantly higher in the core from Hunterston compared to all other sites. Lowest concentrations were found in the core from Kilbrannan Sound. Highest PBDE concentrations in the cores were at slightly variable depths, 4–8 cm from Hunterson, 0–4 cm from the Holy Loch and 4–8 cm from Garroch Head. The BDE209 concentrations at Hunterston and Garroch Head are comparable though maximise at different depths (Hunterston 8–12 cm; Garroch Head 12–16 cm). The source of the high BDE209 concentrations is known for Garroch Head (inputs of sewage sludge) but there is no source known for Hunterston. Overall, it is unclear why the PBDE concentrations at Hunterston are higher than at other sites in Scottish waters and due to the lack of any assessment criteria it is unknown whether these would be a cause for concern.

Monitoring programme in Implementing the Water Framework Directive and the Marine Strategy Directive in the Biscay Bay

Maria J Belzunce

Maria JBelzunce presented the Monitoring Programme that is set up in the Bay of Biscay, along the Basque coast (North Spain), for implementing the WFD and the MSFW. Data series covering a period of 15 years were considered.

The sampling strategy applied is based on the observation that the littoral areas are more impacted than the deep sea. Hence in littoral areas a dense grid of sampling stations is defined while in the continental shelf there are 3 sampling stations.

Along the Basque coast 19 sampling stations are located and a total of 32 sampling stations in estuaries. Main water masses have been identified. In the continental shelf 3 stations are defined at 100–120 m depth and are located in the geographical area of each one of the 3 types of water masses. In littoral stations, water, sediments, fishes, benthos, macroalgae, phytoplankton and biomonitors are sampled. Data series for waters, sediments, phytoplankton and benthos are available for the deep stations.

A series of data figures were presented showing the spatial variability of metal concentrations in sediments and the temporal trends of metal and organic compounds concentrations in sediments. From the figures is observed a contamination problem by As, Hg and Pb both, in littoral and in continental shelf sediments. Zn, Cu, Cd concentrations are higher in littoral sediments comparing with the deep ones. Cr and Ni appear in a similar concentration range in both, littoral and deep sediments. The temporal trends show in general less variability in the deep sediments and lower concentrations than in the littoral samples. Some exceptions to this rule also occur, as for example, L-REF10 deep station shows higher variability and higher metal concentrations than some of the littoral stations.

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

WGMS 2011 identified a need for collaboration with WGBEC (Working Group on Biological Effects of Contaminants) for the settlement of the guidance document on the design of a monitoring programme for contaminants in sediment within the MSFD. Indeed, the design of such a programme is directly related to the way the "good environmental status" will be assessed/defined. WGMS is willing to bring its knowledge and understanding of the sediment compartment to the experts of WGBEC in charge of assessing the suitability of sediment GES targets for contaminants. WGMS would more specifically like to discuss these following issues with WGBEC experts:

- For the design of the monitoring programme for contaminants in sediments within the MSFD, WGMS considers the GES to be met within a given subregion if the average concentration of the strata of that subregion a is below the GES target. The precautionary level used to define the GES should thus be the highest as possible and protect the most sensitive species. A lower protection level in the target value would require a higher number of monitoring sites, which is unfeasible.

- While setting the GES target, WGMS recommend to take into account the composition and nature of the sediment. Exposure assessment should be based not only on total concentration in sediment but also on the availability (speciation) of contaminants, which mainly depends on the composition of the sediment. Contaminants are mainly linked to the fine fraction of the sediment. The presence of fine grain materials and, for example, of condensed organic matter (such as black carbon) with high sorption potential will directly affect the availability and thus the potential risk. As already presented in former reports and also reported in the literature, passive sampling could be a useful tool to assess the sorption capacity of the sediment and thus the availability of contaminants (ref?). The exposure of passive samplers made of polymer materials (such as LDPE, POM and PDMS) to sediments enable to assess the freely dissolved concentration of sampled compounds in pore water. Because this freely dissolved concentration is considered to be the driving force for transport or up-take by aquatic organisms, it is also considered as a measure for the bioavailability.

WGMS suggests to have a common session in this field during the next WGMS and WGBEC meeting in Portugal.

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

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

WGMS would like to propose a joint meeting with selected members of the three working groups (MCWG, WGMS and WGBEC) to set a better further collaboration in the field of passive sampling.

13 Recommendations and Action list

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

14 Chair(s) for 2012

The group has unanimously agreed to the continued chairmanship of Patrick Roose, Belgium, and Lucia Viñas, Spain, for the time being.

15 Date and venue of the next meeting

WGMS is kindly invited by the Instituto Hidrografico of Portugal to have its 2012 meeting in Lissbon. The date needs to be set so that it doesn't conflict with MCWG, and, if possible, coincides with WGBEC.

16 Closure of the meeting

The meeting was closed on Friday, 11 March 2011 at 14:00. Both Chairs thanked the group for their collaboration to a successful meeting and thanked, on behalf of the entire group, Craig Robinson and his 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 Lucia Viñas, Spain met in Aberdeen, UK, 7–11 March 2011 to:

1. **Opening of the meeting**
2. **Adoption of the agenda**
3. **Spatial design of a regional monitoring programme for contaminants in sediments:** 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. subregions of the OSPAR Regions) within the period 2010-2020, with the major effort in 2014-2020. The guidance should address:

- 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
- 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. (OSPAR request 2011/2)

4 **Sediments monitoring**

Review and comment on the report of the 2010 meeting of OSPAR/MON in relation to sediments.

5 **Review information relevant to the regionalisation of pivot values and background concentrations of contaminants in sediment.**

6 **To continue work on the uncertainty in data assessments arising from the selection of co-factors**.

7 **Continue collection of data and develop background concentrations for alkylated PAHs**

8 **Passive Sampling**

8.1 Provide a document discussing the different passive samplers presently used.

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

8.3 Report ongoing and new projects involving passive sampling:

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

10 **TIMES papers on the analysis of dioxins and PCBs**

11 Plenary presentations

12 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 will report by 15 April 2011 (via SSGHIE) for the attention of SCICOM and ACOM.

Annex 3: WGMS draft terms of reference for 2012

The **Working Group on Marine Sediments in Relation to Pollution** (WGMS), chaired by Patrick Roose, Belgium, and Lucía. Viñas, Spain, will meet in Lisbon, Portugal, DATE (to be announced) March 2012 to:

Sediments monitoring

a) Develop 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;

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.

Background concentrations

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

Passive Sampling

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

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

h) To report on ongoing and new projects involving passive sampling.

Miscellaneous

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

WGMS will report by 15 April 2012 (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	a) This is a direct request from OSPAR. b) Anticipating that the report of the proposed 2011 assessment will be available before the meeting, WGMS can review and comment the progress made; c) This work has direct implications for the OSPAR/MIME assessment process where pivot values play an important role. Current work shows there are regional differences between pivot point values and the need therefore arises to evaluate pivot point values submitted for use in OSPAR trend assessments, whith emphasis on the validity of the supporting evidence and the area these pivot values apply to. Also, there should be sufficient spatial coverage for this area, and sufficient repeatability. WGMS should be requested to define what is sufficient by referring to the original dataset used to produce the OSPAR pivot values (OSPAR, 2008) next year d) The uncertainty associated with the use of co-factors has potentially a significant impact on data assessments. WGMS will investigate this and advise accordingly. e) 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. f) 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. g) Partition coefficients are used as a normaliser for organic contaminants by OSPAR MON. However, sediment sorption cannot always be adequately represented by the Koc. WGMS will further investigate the use of passive samplers as an alternative. j) 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. i) Response to internal requests from ICES.
Resource requirements:	None required
Participants:	The Group is normally attended by some 20 members and guests.
Secretariat facilities:	None.
Financial:	No financial implications.
Linkages to advisory committees:	ACOM
Linkages to other committees or groups:	WGBEC, MCWG
Linkages to other organizations:	OSPAR, HELCOM

Annex 4: Recommendations

Recommendation	For follow up by
1. 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
2. WGMS recommends that CPs assess pivot point value concentrations against the OSPAR value and, if significantly different, nominate these values with precision for their regions.	OSPAR

Annex 5: Action list

AGENDA ITEM		
3	To formally invite a GIS expert from the Instituto Hidrográfico to attend in order to provide support during the meeting.	WGMS chairs
3	To check the GIS platform used by Instituto Hidrografico.	Carla
3	To check sediment composition for their "region" and to send Carla GIS-based maps of sediment grain size to the next meeting in order to define strata for all OSPAR regions.	All members
3	To ask for ICES assistance in getting the information from the station dictionary	WGMS chairs
3	To provide the sampling locations of their national monitoring programmes in an agreed GIS format and to see how existing monitoring programmes fit into the structure	All members
3	To invite a statistician to assist WGMS on different issues related to the development of spatial monitoring guidance next year: Spatial coverage Number of samples that are representative of the sampling area for comparison with GES, BACs, time trends Frequency of sampling	WGMS chairs
3	To contact Rob Fryer and inquire if he is able to join next year meeting.	WGMS chairs
3	Claire to provide a template to all members by end of May for contaminant concentrations from the same sample in different size fractions in order to check if the uncertainty of back calculation from sieved to total concentrations is acceptable	Claire
3	To provide Claire data by December to investigate the relationship between total and sieved concentrations	All members
3	To provide information on additional supporting parameters (such as redox conditions) that may influence the mobility of contaminants.	All members
3	To develop some examples to allow two possible approaches of assessing concentrations against GES to be compared and present them for discussion at MIME 2011	Rob Fryer
3	To investigate whether the pivot point normalisation process can be reversed.	All members
7	To provide new data on background concentrations of alkylated PAHs and dioxins	All members (mainly Céline Tixier, Craig Robinson, Ingemar Cato and Lucia Viñas)
8	WGMS members are encouraged to bring new information related to the use of passive samplers in environmental monitoring, particularly related to sediment.	All members
8	To contact Foppe Smedes to see whether he is willing to continue the work related to items 8.1 and 8.2 in the agenda.	WGMS chairs
12	Contact the chairs of WGBEC to explore the possibility of a common session during next year's meetings in Portugal.	WGMS chairs
12	Investigate a joint meeting with selected members of the three working groups (MCWG, WGMS and WGBEC) to set a better further collaboration in the field of passive sampling.	WGMS chairs

Annex 6: Guidance to monitoring contaminants in marine sediments from offshore and coastal areas in the Baltic Sea

1. Introduction

This guidance on the design of a regional (part of a subregion) monitoring programme for contaminants in sediments is aimed to be used in several regions to explain, whether good environmental status (GES) has or has not been achieved on a larger regional scale (e.g. subregions of the OSPAR and HELCOM Regions) within the period 2010–2020, with the major effort in 2014–2020.

The objective of this monitoring program of sediment is to determine the status and/or long-term trends of toxic contamination in both open sea areas throughout the member state´s territorial waters and Exclusive Economic Zones (EEZ), and/or member states coastal waters. Furthermore, the open sea programme should also be regarded as a complement to similar coastal monitoring programs run by regional authorities as well as local recipient monitoring programs carried out in areas where industries and municipalities are using coastal areas as a recipient for discharging treated waste- and sewage water.

The monitoring programme, described below, has mainly been designed in line with the outlined programme agreed upon by the HELCOM MONAS *ad hoc* Working Group on Sediment Monitoring of the Baltic, the Kattegat and the Belt Seas. In addition to this it is recommended that the monitoring programme also meet the requirement of the MORS-PRO radioactivity monitoring in sediments (HELCOM).

2. Bottom dynamic

It is essential to understand and take into consideration the various underlying sediment dynamic processes in both the open North Sea and the Baltic Sea, and in coastal waters, when a sediment monitoring programme will be designed. This in order to avoid selecting sampling sites unsuitable for the tasks. For information on sediment dynamic processes in relation to studies of contaminants in sediments, the reader is advised to consult the ICES Cooperative Research Report No. 308 - Sediment dynamics in relation to sediment trend monitoring.

3. Selection of sampling stations and sampling sites

The primary criterion for selecting suitable sites for monitoring, is to find places that are representative of large open sea areas and to avoid local, near coastal contamination close to urban areas. Another primary criterion is to use areas where there is an undisturbed, continuous and recent deposition of fine-grained (<63 μm) sediments. With undisturbed sediment is meant no bioturbation, no physical disturbance from waves and bottom currents action, and/or anthropogenic disturbances due to human activities (e.g. trawling, anchoring). Such places are in general found in depressions or basins, often with anoxic bottom conditions.

To meet these criterions, the most useful places evenly distributed within a subregion has to be identified prior to sampling activities. The following steps have to be undertaken:

- <u>By early planning,</u> areas likely to be used, may be identified. Information on the bottom topography will be found in sea-charts, accessible multibeam data and other relevant bathymetric information. This information has to be combined with accessible seabed sediment information (e.g. marine geological maps and other accessible information, e.g. various sediment and bottom-fauna studies, etc.).

- Areas likely to be used, have to be investigated with various hydro-acoustic techniques such as side-scan sonar, subbottom profiler (3.5/7.5 kHz) and echo-sounder (35/200 kHz). Based on the information retrieved, limited areas suitable for monitoring may be identified and chosen for the next step.
- Ground-truthing is necessary as quality control of all remote sensing analyses, e.g. side-scan sonar images and other types of back-scatter data never give enough detailed information of the sediments. Thus, ground-truthing has to be carried out by sampling and examination of the sea-bed sediment at all chosen possible monitoring sites. Prior to sampling, it is desirable, that the bottom condition at the site is inspected with an underwater video-camera. This, in order to clarify that the sampling site not has been disturbed by activities such as trawling, anchoring, etc.
- The final sampling aimed for monitoring of the environmental chemical status can be carried out by either a spatial sampling in selected places over the whole region or by selecting a small number of the most optimal and for the region most representative bottom areas. In both cases the above listed demands should be fulfilled. In the latter case the following sampling procedure is recommended to be undertaken.

Within each selected bottom area, a sample station has to be placed at an ultimate position. The sample station is defined as a circle with a radius of 50 metres and with the master core-site placed in its centre. Within the circle and around the master site six more coring-sites (slave sites) has to be randomly chosen. In total, seven sites will be sampled at each station (circle), and at each core-site enough sediment-cores has to be taken to get the amount of sediment needed for analyses.

To get best control of the sediment used for chemical analyses it is desirable to x-ray one core from each site, e.g. in a digital x-ray-scanner (Cato *et al.* 2000). If the sediment core is unconsolidated, the sediment core has to be x-rayed in an upright position with bottom-water on top of the sediment. If the sediment is strongly bioturbated or of other reasons disturbed a new sampling site has to be selected. The radiographic technique provides digital records of the internal structures of the sediment cores and this is of ultimate importance when evaluating geo-chemical records. One core from the site has to be cut longitudinally into two parts, photographed with digital technique and examined visually.

4. Coring and subsampling

One sediment core, taken at each site, has to be carefully treated to remove the overlying bottom water from the sediment surface, sliced in an upright position in a core-cutter into a suitable thick slice from the surface (e.g. 0-1-cm), and transferred to plastic jars and stored frozen until later analysis of major and minor elements, organic carbon, nitrogen.

One core from the master site, sliced in 1-cm thick subsamples from top to bottom, is needed for isotope analyses (e.g.137Cs, 210Pb) aimed for dating and estimation of the accumulation (deposition) rate for the station. When isotope analyses have been carried out, the same samples can be used for analyses on e.g. major and minor elements, organic carbon and nitrogen. The isotope analyses and estimation of the sedimentation rate is carried out once for each station and is not needed to be repeated if the station is used for trend monitoring.

One sediment core from each site, and with the same slicing technique, only the topmost centimetre (0-1 cm) may be taken, pooled, mixed and transferred to a glass jar. The sediments put into glass jars for each site then has to be mixed and homogenized into one large sample representing the entire station, and stored frozen until later analyses of elements, organic carbon, nitrogen and organic contaminants. As the latter analyses are the most expensive, when the WFD- and MSFD directives have to be met, these substances can be considered only to be analysed on a pooled-sample to reduce the costs. This, however, means that the data for organic contaminants will be single determinations for each site and statistical handling of the data is impossible.

The inhomogeneity of the sediments within a station will be sorted out by statistical treatment of the seven surface samples by using the major and minor elements and organic carbon. Seven samples are the minimum of samples (data) needed to achieve a statistical probability. The result could be applied to the organic contaminants if only a pooled sample is analyzed.

The number of cores, subsamples and amount of sediment needed depends on the task and the target that has to be achieved.

Annex 7: Technical minutes of the Review Group MON2 2011 (RGMON2)

Review of the 2011 Report of ICES Working Group on Marine Sediments in Relation to Pollution.

6 May 2011

Reviewers: Paul Keizer, Canada (Chair); Jose Fumega, Spain; Michiel Kotterman, NL; Jordi Dachs, Spain

Chair WG: Patrick Roose, Belgium, and Lucia Viñas, Spain

Secretariat: Claus Hagebro

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

This report provides technical comments on the preliminary draft advice from WGMS on the request from OSPAR to provide advice on the spatial design of a regional monitoring programme for contaminants in sediments:

> 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.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
>
> 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

RGMON2 realised that the material in the WGMS 2011 report was very preliminary in nature, the intention being to provide the requested advice to OSPAR in June of 2012. The comments of RGMON2 are therefore focused on the general content of the WGMS2011 report rather than the detailed content. RGMON2 hopes that these comments will assist WGMS with its intersessional work on this guidance document. This document uses the same organisation as the WGMS 2011 report.

Spatial design of a regional monitoring programme for contaminants in sediments

The first reaction to this request from OSPAR should be "what is GES?" The definition of GES will answer or provide the essential guidance to many of the issues that need to be addressed. OSPAR cannot expect a definitive response to this request until GES with respect to contaminants in sediments is clearly defined.

1) What is the scale?

The recommendations in the last paragraph, presumably address open water monitoring. The approach is applicable where there is no *a priori* information of the potential "areas of interest." Potential "areas of interest" would be defined by existing information on the distribution of contaminants in sediments and/or information on point sources of contaminants. In addition water circulation models in concert with modelled particle tracking can help define "areas of interest". However the scale and subsequent design of the monitoring program will depend upon how GES is defined and specifically how goals and targets are defined.

In terms of hydrophobic organic pollutants, they tend to be associated with organic matter and black carbon pools of sediments. A correct characterization of sediments in terms of organic matter content is needed. It is not enough to only consider the "grain size".

The OSPAR division of sub-zones is arbitrary and each zone contains a considerable variability. The variability will be higher close to the coastal zone. This variability needs to be assessed. The division between the 12 nautical miles and outside them is also arbitrary. A division of continental shelf sediments and rest of sediments would be more relevant.

2) What is GES?

As noted above the answer to this question is essential to the request. While the draft text is useful, ultimately this text will have to address the specific definition that is agreed upon by Member States.

3) Should the design address solely assessment against GES, or also include assessments against background and trend monitoring?

Based on the experience of OSPAR definition of GES for some chemicals may have to be based on trend analysis and/or comparison with background values. The experience of OSPAR with its 2 QSRs and HELCOM with its Baltic Assessment should provide the basis for guidance on optimising monitoring programs based on the intended assessment procedure. It is unlikely that one assessment procedure will be optimal for all areas. For example, in some areas there may be sufficient information to define EACs, in other areas it may be possible to define background concentrations, while in other areas the only reasonable assessment tool could be temporal trends.

4) Should we only look at silty areas, or should we also include sandy areas?

The following statement needs to be given careful consideration:

"However, much of Region II (for example) is relatively coarse sediment and therefore, in order to demonstrate GES convincingly on the sub-regional scale, it is important to have some samples from the areas of coarse sediment and not only in the depositional areas of finer sediment."

It is not clear why sampling where we do not expect to find contaminants is either useful or a defensible expenditure of scarce resources. Again the argument here will be influenced by the definition of GES. Will the focus be on areas of known, expected, or predicted contamination or will some type of spatial average be used? For example, with respect to Region II if fine grain sediments are only found in 5% of the total area will the contaminants in those sediments be considered as distributed over all of Region II? We suspect/hope not and the focus would be on the fine-grain sediments.

5) How many strata? How many samples in a stratum?

This draft text seems to apply to offshore areas where there are known sizable areas of fine-grain sediment. This text is a useful exploration of some of the concerns but ultimately the official definition of GES will need to be addressed. It would be informative to have a discussion, based on the OSPAR experience with various targets, of the feasibility of defining GES targets as mean concentrations. What about areas where there are well-known point sources?

6) What fraction of the sediment should be analysed?

An interesting discussion but as the first sentence in the section notes the answer to this question depends upon the definition of GES.

Hydrophobic organic pollutants will be concentrated in the sediment fraction that contains the most organic and black carbon. An initial assessment of organic and black carbon provides guidance for assessing content of organic pollutants.

7) How frequently should sediment monitoring be undertaken?

The argument in the first paragraph is not well-founded. Using the example provided, after 1 year 20% of a sample would represent new input, etc. The argument for frequency should be based on knowledge of the dynamics of the contaminant source and the dynamics of the contaminant once it reaches the sediments.

It seems unreasonable to expect a definitive response to this request until GES as it relates to contaminants in sediments is clearly defined.

Annex 6: Guidance to monitoring contaminants in marine sediments from offshore and coastal areas in the Baltic Sea

This document was considered for information by WGMS and therefore the following comments are not directed at the document itself but rather at its relevance in the development of the advice.

This document provides some useful guidance however the focus on the need to take samples from areas with undisturbed fine grain sediments is perhaps too limiting. One of the general goals of the MSFD is to protect the health of marine organisms but the suggested site selection would essentially avoid areas that are frequented by marine organisms; i.e. undisturbed, no bioturbation. We would stress the need to remember the overall goals of the MSFD or any other contaminant monitoring program.

Presumably sampling methods other than coring will be considered.