

ICES WGMS REPORT 2014

SCICOM STEERING GROUP ON HUMAN INTERACTIONS ON ECOSYSTEMS

ICES CM 2014/SSGHIE:10

REF. SCICOM, ACOM

Report of the Working Group on Marine Sediments in Relation to Pollution (WGMS)

3–7 March 2014

ICES Headquarters, Copenhagen, Denmark



ICES
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International Council for
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Recommended format for purposes of citation:

ICES. 2014. Report of the Working Group on Marine Sediments in Relation to Pollution (WGMS), 3–7 March 2014, ICES Headquarters, Copenhagen, Denmark. ICES CM 2014/SSGHIE:10. 68 pp. <https://doi.org/10.17895/ices.pub.8983>

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Executive summary

The Working Group on Marine Sediments in Relation to Pollution (WGMS) met from 3 to 7 March in Copenhagen, Denmark. The meeting was chaired by Craig Robinson and Lucía Viñas and attended by 15 scientists (plus a further two WebEx contributions) from ten countries. The meeting was held at ICES Headquarters concurrent with the annual meetings of the Marine Chemistry Working Group (MCWG) and the Working Group on Biological Effects of Contaminants (WGBEC).

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, including two sessions held jointly between the three groups (on passive sampling of contaminants and on marine litter).

OSPAR requests on a possible method to determine the geographic representativeness of existing sediment monitoring stations and the review and update of the Technical Annexes of JAMP Guidelines for Monitoring Contaminants in Biota and Sediments, were the main tasks at the meeting.

With regard to the method for determining the geographical representativeness of sediment stations, three methods were mainly explored. One based on investigating the variability of existing data in relation to geographic scale, the second using bubble plots overlaying a map, and the third based on a geostatistical method, krigging. In conclusion, the group were unable to recommend a method for determining spatial representativeness although, of those investigated, krigging appears best suited.

In response to requests by OSPAR, the revision and update of the technical annexes 4 and 6 to the JAMP Guidelines for Monitoring Contaminants in Sediments was addressed jointly with MCWG. The changes were relatively minor, but included reference to new analytical methods, such as pyrolysis for the determination of Hg.

There was also a request from OSPAR on finalising the spatial design for region scale monitoring. The guidelines for region scale monitoring were already finished last year and the ICES advice based on those was forwarded to OSPAR. The advice received some criticism from the Netherlands particularly regarding the availability of sediments with >20% fine fraction (<63 µm), whether or not to sieve the samples, and a lack of normalisation procedures in data assessment. In discussion, WGMS recognised that a pragmatic approach would be required and that sediments with less than 20% fine fraction could be used, and that data from sieved fractions can be used if the obtained concentration data are converted (based upon the fine fraction content) to total sediment concentrations for comparison with assessment criteria expressed on a total sediment basis.

During the meeting there were also some joint sessions with WGBEC and MCWG on Marine Litter, Ocean Acidification and Passive Samplers. In order to keep the momentum of the ICES Workshop on the application of Passive Sampling and Passive Dosing to marine media (WKPSPD), the three Working Groups agreed to work towards the long-term goal of developing environmental assessment criteria and agreed methodology (e.g. TIMES papers).

WGMS also discussed extensively on the ToRs proposed for the next three years and concluded that these ToRs will mainly include, apart from specific OSPAR and ICES requests, issues related to passive sampling, the possibility of using modelling to explain spatial distribution patterns of contaminants in sediment, deep sea sediment

monitoring, the impact of renewable energy devices and other emerging issues such as microplastics or deep sea mining.

1 Opening of the meeting

The 33rd meeting of the Working Group on Marine Sediments in relation to Pollution was opened by the two co-Chairs who welcomed the participants to Copenhagen and outlined that this meeting was to be held concurrently with the annual meetings of the Working Group on Marine Chemistry (MCWG) and the Working Group on Biological Effects of Contaminants (WGBEC), in order that joint sessions could be held on the subjects of marine litter, ocean acidification and passive sampling.

2 Adoption of the agenda

The agenda was accepted without modifications. The most important items in the agenda were to finalise the guidelines for region scale monitoring and two special requests from OSPAR: one regarding the recommendation of a method to determine the geographic representativeness of existing sediment monitoring stations and one on the review and update of the Technical Annexes of JAMP Guidelines for Monitoring Contaminants in Biota and Sediments.

3 Sediment monitoring

3a Finalise spatial monitoring guidelines

At the 2013 meeting in Lowestoft the WGMS had developed guidelines for a spatial design for regional scale monitoring of which results were considered suitable to assess if good environmental status (GES) for chemical contaminants is achieved, i.e. meeting MSFD criteria. The aim of the WGMS 2013 guidelines was to be able to conduct the MSFD status assessment at the (sub-)region scale and not on a local, single station, scale. Furthermore, it was stressed, that the monitoring design developed by WGMS 2013 was not intended to allow conclusions related to specific contaminant sources or pathways. In order to avoid confusion with the existing OSPAR spatial monitoring that aims at identifying areas of enhanced concentrations and location of sources, WGMS will hereafter refer to this design as a region-scale monitoring programme, rather than spatial monitoring. It was pointed out that derivation of measures in order to improve the environmental quality related to contamination generally requires results from the trend monitoring or a spatial monitoring.

The guidance provided by WGMS2013 advised that such region-scale monitoring could be limited to deposition areas and that the deposited sediment would be representative for larger supplying areas. As existing assessment criteria were based on information on toxicity in whole sediment, WGMS 2013 recommended that the monitoring includes contaminant concentrations in total sediment without normalisation but should be limited to sediment samples with contents of fines >20%. The group defined several such areas in/around the southern North Sea based on data for sediment composition collected from different sources and modelling. Case studies with existing data from the ICES database were used to assess the variability and subsequent power analyses to estimate required number of samples to statistically confirm compliance with EAC or ERL.

The work of the WGMS formed the basis of the ICES advice formulated by SSGHIE in October 2013 and forwarded to OSPAR for consideration in MIME (ICES, 2013). WGMS 2014 recognised that this advice included some amendments compared to the recommendations provided by WGMS 2013. In addition to the advice given by

WGMS 2013 to restrict monitoring, for the purpose of quality assessment, on areas with fine-grained sediments, the ICES advice also included that fine fractions ($<63 \mu\text{m}$) could be used. WGMS have difficulties with the concept of comparing data from sieved sediments with assessment criteria (e.g. ERLs/EACs) for total sediments. The group, however, recognised that a pragmatic approach would be that where data from sieved fractions are used in GES assessments, then the comparison with assessment criteria should be like-for-like and this could be achieved by converting concentration data from sieved sediments to a total sediment concentration by correcting for the fine fraction content of the original sample. The group considers that the main principle is that, for region scale assessment, the sampling should be conducted in depositional areas. The group also recognises that this approach is limited to region scale assessments and is not informative on specific contaminant sources. This situation arises because of the difficulty caused by having assessment criteria defined on a total sediment basis.

The Netherlands has further reviewed the guidelines from WGMS 2013 and made the document available to the WGMS 2014 meeting (Annex 4). The document did not dispute the statistical approach the spatial design for monitoring regions was based on, but expressed doubts on the practical feasibility and suggested to include alternatives that would prevent failing application and to make a better use of existing data. Main comments in the Dutch review document were:

- ICES advise that only total sediments with a content of fines over 20% should be sampled. It was strongly doubted that these would be sufficiently available. Samples taken by the Netherlands rarely exceed the 10% fines, although the maps produced in previous years showed (e.g. in the Oyster Grounds) sediments with a sufficiently high amount of fines. This would/could lead to costly resampling if insufficient numbers of samples meeting the criterion of having a content $>20\%$ fines were collected.
- Further, the Netherlands advised to use with caution the variability in concentrations estimated by WGMS2013 in their case studies for the North Sea as this was largely derived from measurements in sieved fractions recalculated to total sediment concentrations by multiplying with a factor of 0.3. This approach would under-estimate the actual concentration variability of the unsieved sediments by a factor of 2 and therefore overestimates the power of the scheme, which may have led to an underestimation of the required number of samples.

Based on these observations the review by the Netherlands suggested that, in addition to what was recommended in the ICES advice, the advice should allow the use of recalculated sieved fractions as an alternative. The review suggested to perform a trial to investigate the validity of such an approach, although, in reality, the case studies confirmed that this approach would work, as they were dominantly based on such data. WGMS 2014 considered this approach (back-calculation to whole sediment, based on the grain size data) to be a valid means of including concentration data from sieved samples in assessments for GES and suggests to MIME that they include it in their revision of the JAMP Guidelines of Monitoring Contaminants in Sediments.

The group took note of these comments and discussed whether monitoring should be restricted to samples with $>20\%$ fine sediments or whether, if the samples did not meet this criterion that they should be analysed or included in the assessment. This discussion reflected uncertainty in the accuracy of the sediment grain size maps, alt-

though it was considered that the identified areas would be the depositional ones and thus are the best areas for inclusion in the region assessment.

This would also be cost effective as it can make use of the existing spatial and temporal trend monitoring data and would even allow some retrospective assessment.

In further discussion, concerns were expressed over the general approach to the development of assessment criteria for sediments assuming that toxicity would be related to whole sediment concentrations, and therefore that the geochemical composition and grain size distribution could be ignored. WGMS 2014 decided to review new information on sediment assessment criteria and their applicability at its next meeting.

Reference

ICES, 2013. OSPAR request on spatial design of a regional monitoring programme for contaminants in sediments. *ICES Advice 2013*, Book 1, 1.5.6.8.

3b Review and comment on the report of the 2013 meeting of OSPAR MIME in matters concerning sediments

At its 2013 meeting, MIME decided that experts from Denmark, Germany and UK (with a possible 'peer-review'-type contribution for the Netherlands' expert) should aim to provide a consolidated proposal updating the JAMP Guidelines for Monitoring Contaminants in Sediments. No consolidated proposal was available to WGMS2014, although the group were able to review the first draft revision prepared by MIME 2013 (Annex 13, Appendix 2 to MIME 13/8/1-E and in HASEC 14/6/6-E document). MIME 2013 had started to include the ICES 2013 advice on region scale monitoring for assessing the environmental quality of MSFD (sub-)region based mean concentrations of contaminants in sediments against assessment criteria. WGMS considered that some clarification with regard to § 4.2 (MIME-document) and § 4 (HASEC-document) would be helpful. There seems to be some confusion at OSPAR with regard to the spatial design for a region scale monitoring programme for the purpose of assessing GES (ICES advice from 2013) and spatial monitoring aimed at identifying areas with enhanced contamination and contaminant sources (e.g. the existing CEMP). WGMS 2014 recommends a clear differentiation between MSFD-monitoring, trend-monitoring and OSPAR spatial monitoring by structuring the guidance document to better reflect these different objectives and naming the MSFD-related monitoring to "region scale monitoring programme" (c.f. ToR 1a).

WGMS considered that the ICES advice on the JAMP sediment monitoring guidelines should be further developed. In the course of the discussion, WGMS compiled a few recommendations for further revision:

- 1) As stated earlier, in the guidelines, the "regional assessment of good environmental status" should be renamed to "region scale monitoring" in order to avoid confusion with the existing spatial OSPAR monitoring;
- 2) For reasons of clarity, the order of some paragraphs of the existing main text of the JAMP Guidelines should be rearranged and should provide advice according to the different types of monitoring, where appropriate. Steps that are in common for all monitoring objectives, i.e. sample storage, should be retained;
- 3) The details of advice should be on a similar level for all types of monitoring, as far as possible. In the existing JAMP guidelines some gaps of information were identified for some types of monitoring;

- 4) The advice given in the general text of the JAMP Guidelines should be in line with the advice provided in Technical Annexes. Especially the main text should be in line with the advice given in Technical Annexes 2 and 5. Some discrepancies were identified, especially between the general text and Technical Annex 5;
- 5) The JAMP sediment guidelines are consistent with, and reflected in the Water Framework Directive CIS Guidance Document 25 with regard to monitoring of sediment and biota.

4 Special request on whether to recommend a method to determine the geographic representativeness of existing sediment monitoring stations

This request was noted as coming from MIME 2012, and although several members of WGMS were present at MIME, they could not recall discussion of this subject and were unable to assist in interpreting the meaning of the question. As a result, WGMS 2014 had several different interpretations of the question that it decided to attempt to answer.

Q1: Suitability of sediment transport models to inform on the required spatial distribution of monitoring stations

Whilst many research groups are working on the development of sediment transport models, the opinion of WGMS was that these are not currently able to be used to trace the source of contaminated sediments at a given location, nor therefore able to describe (with sufficient detail on a region scale) where sampling stations should be located. Existing understanding hydrodynamic models can predict the dispersion of suspended particles from riverine input (e.g. Ferrer *et al.*, 2009), but require input on the contaminant concentrations of these before they can be used to model the input of contaminants to a given sampling area.

Ferrer, L., Fontán, A., Mader, J., Chust, G., González, M., Valencia, V., Uriarte, Ad., Colins, M.B. 2009. Low-salinity plumes in the oceanic region of the Basque Country. *Continental Shelf Research*, 29, 970-984.

Q2: Can we use existing monitoring stations to say whether we have GES?

In keeping with the ICES 2013 advice, the existing monitoring stations that are in areas of fine sediment can be used for regional-scale assessments of compliance with GES thresholds based on whole sediment concentrations (i.e. not normalised or sieved). As detailed in the ICES 2013 advice, it may be necessary for samples to be obtained from additional stations within a stratum in order to obtain sufficient statistical power to assess concentrations against the assessment criteria (e.g. ERL / EAC). It should be noted that any additional sites would only be required to be sampled once within the 6 year reporting cycle of the MSFD. This is to allow an assessment of GES; for trend monitoring, the existing stations should continue to be sampled at the frequency required by that monitoring programme. In contrast to the 2013 ICES advice on monitoring for GES, time trend monitoring usually uses data from sieved samples. In order to avoid gaps in time series, or the collected samples being analysed twice (sieved and unsieved), data from sieved samples can also be used for the GES assessments, but in that case the concentrations must be corrected for the fraction of the sample that was not analysed, i.e. concentrations should be back-

calculated from the fine fraction concentration to a whole sediment basis to allow comparison with Assessment Criteria that are based upon whole sediments.

Q3: How does concentration variability relate to the size of a geographic area / strata?

Due to time constraints, this question was addressed by sub-group after the meeting. To attempt to answer this question, two offshore areas (>12 km from the coast) of the southern North Sea were selected (Figure 4.1). Area AB was the central southern North Sea, whereas area C was predominantly the Belgian sector. To assure minimal influence of grainsize composition normalised contaminant data (5% AI for metals 2.5% TOC for organics; sieved samples) were obtained from the ICES database. Data for sampling stations indicated in areas AB and C were isolated from the same dataset as was used in the kriging exercise (see below). To investigate the effect of spatial scale on variability, Area AB was halved into A and B, and then area B quartered and a weighted (number of observations) linear regression conducted of Cd and of Hg concentration variability (relative standard deviation) as 0251664384a natural log function of the area ($\log_e \text{ km}^2$) in the different sized boxes (Table 4.1).

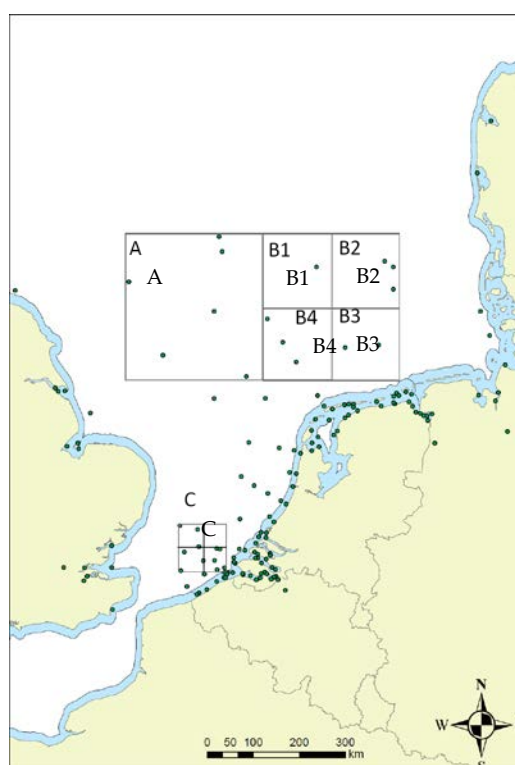


Figure 4.1. Sediment sampling stations, and boxes used to investigate variability of data on different spatial scales. Inshore areas (<12 km from the coast (blue) were avoided).

Table 4.1. Cadmium and mercury concentrations (mg/kg, normalised to 5% Al) of sieved sediments in different sized areas of the southern North Sea. See Figure 4.1 for locations of the areas.

Area ID	Area (km ²)	n=	Cd			Hg		
			Mean	SD	RSD (%)	Mean	SD	RSD (%)
AB	190000	15	0.260	0.367	141.2	0.112	0.087	77.8
A	95000	6	0.246	0.117	47.5	0.088	0.021	24.2
B	95000	9	0.269	0.477	177.0	0.127	0.111	86.9
B1	23750	1	0.134			0.068		
B2	23750	3	0.595	0.818	137.6	0.194	0.190	98.0
B3	23750	2	0.129	0.038	29.6	0.125	0.005	3.9
B4	23750	3	0.083	0.006	7.1	0.082	0.033	40.5
C	10690	11	0.436	0.186	42.7	0.183	0.071	38.7
C1	2673	3	0.294	0.108	36.7	0.160	0.053	32.8
C3	2673	5	0.518	0.225	43.4	0.234	0.068	28.9
C4	2673	3	0.439	0.114	25.9	0.121	0.016	13.3

Area AB covered 190 000 km², contained 15 sampling sites and had an RSD on the Cd data of 141%; whereas area C covered 10 690 km², contained 11 sampling sites and had an RSD for Cd of 42.7%. Thus, although there was a similar number of stations in each area, the variability was less in the smaller area. Dividing area AB in half (95,000 km² each) there were 6 sites in area A (RSD=47.5%) Plotting the variability (RSD) against the geographical area of each box shows a tendency to lower variability in smaller area (Figure 4.2). Although, whilst the three smallest areas (C1, C3, C4) had a similar level of variability (25–45% RSD), the three boxes in area B containing sampling stations (B2, B3, B4) had very dissimilar variability (7–135% RSD). The weighted regression of the Cd concentration variability (RSD) against the natural log of the area showed a significant positive relationship ($RSD = -196 + 27.4 \ln(\text{km}^2)$; $p=0.017$, $\text{adj-}R^2=0.47$), as did that for Hg ($RSD = -68 + 11.7 \ln(\text{km}^2)$; $p=0.040$, $\text{adj-}R^2=0.36$). However, it should be noted that neither of these apparent relationships are significant if Area AB is removed from the models. Knowledge on the variability of concentration data for many more boxes of different spatial scales are required in order to have confidence in defining a relationship between variability and spatial area.

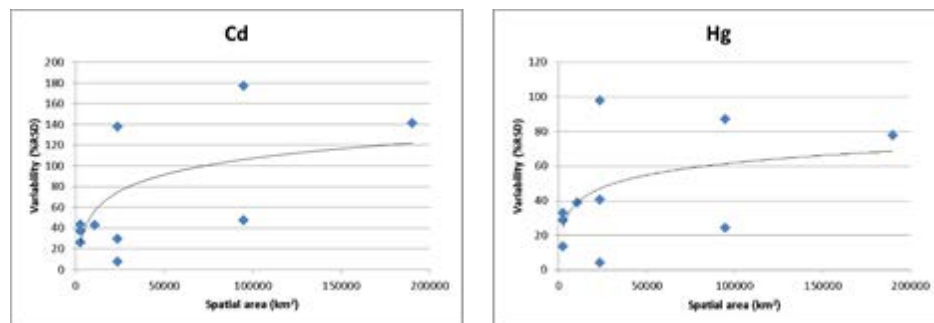


Figure 4.2. Effect of spatial area on variability (relative standard deviation) of 5% Al-normalised Cd and Hg concentrations in sieved sediments from the southern North Sea. Fitted line is the weighted (number of observations per point) log_e regression.

Q4: Can we say how big a geographical area each sampling station represents?

A **graphical method using bubble plots** can be used as a “quick and dirty” investigative tool. Plotting concentration data (raw and normalised) as bubble-plots overlaid on maps is a simple way to visualise the degree of variability in a given area. To demonstrate this, sediment contaminant and co-factor concentration data for sieved sediments from the southern North Sea were obtained from the ICES database (1998–2009) and overlaid on maps also indicating the areas of fine sediment (>20% silt/clay) identified in the ICES 2013 advice on sediment monitoring for GES purposes. Figures 4.3–4.5 show mean concentrations (mg/kg dw for metals and µg/kg for organic compounds) of Hg, CB52 and TBT after normalizing to 5 g kg⁻¹ Al (metals) or to 2.5% OC (organics). These contaminants are of anthropogenic origin (CB52, TBT), or predominantly so (Hg), and the plots appear to show that fine-fraction sediment concentrations in offshore depositional areas (coloured blue) are similar to those in the fine fraction of the wider offshore area, although this may be due a scaling effect. It is apparent that, as expected, concentrations in inshore areas of fine sediment tend to be much higher and more spatially variable than offshore.

In contrast, the bubble plots of substances for which there are significant natural background concentrations (e.g. fluoranthene, Cd and Pb; Figures 4.6–4.8) show large differences in the diameter of the bubbles between the offshore areas of fine and coarse sediment and indicate that for such substances, samples collected in the areas of fine sediment may not be reflective of the offshore southern North Sea. This could be assumed to be due to the relatively small ratio of anthropogenic signal to natural background concentration. Thus, concentrations in the fine fraction of samples in offshore depositional areas may be representative of sieved samples from the wider area for some substances, but not for others.

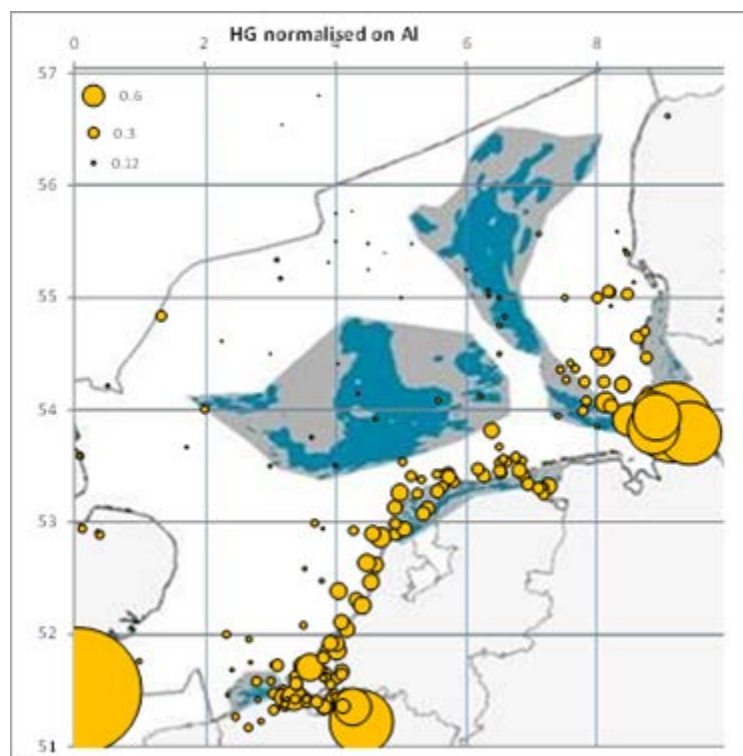


Figure 4.3. Bubble plot of sediment Hg concentrations in the southern North Sea (mg/kg dw, normalised to 5% Al). The blue areas were identified in the WGMS 2013 report as having <20% silt-clay fraction (<63 µm).

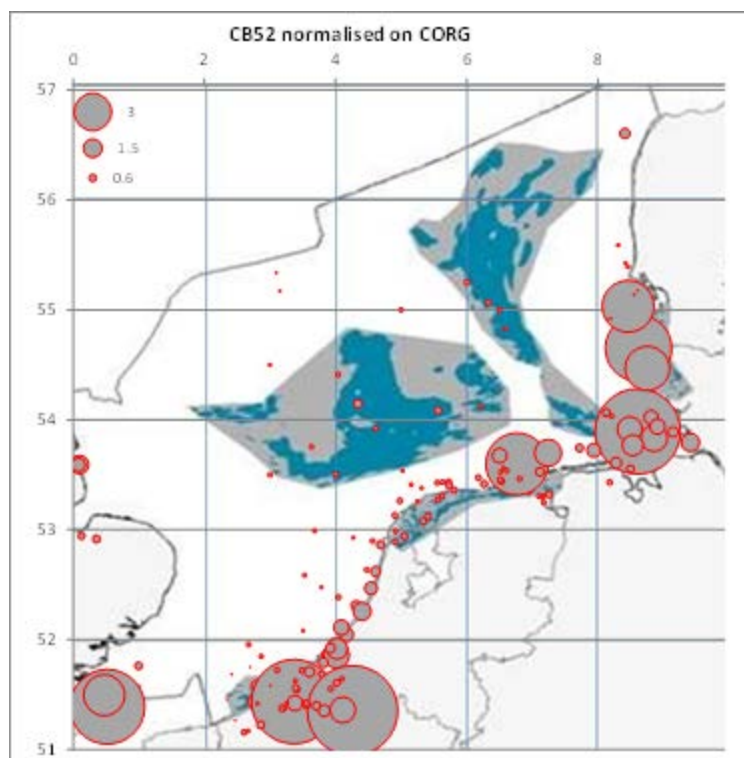


Figure 4.4. As Figure 4.3, but for CB52 concentrations (µg/kg dw, normalised to 2.5% total organic carbon).

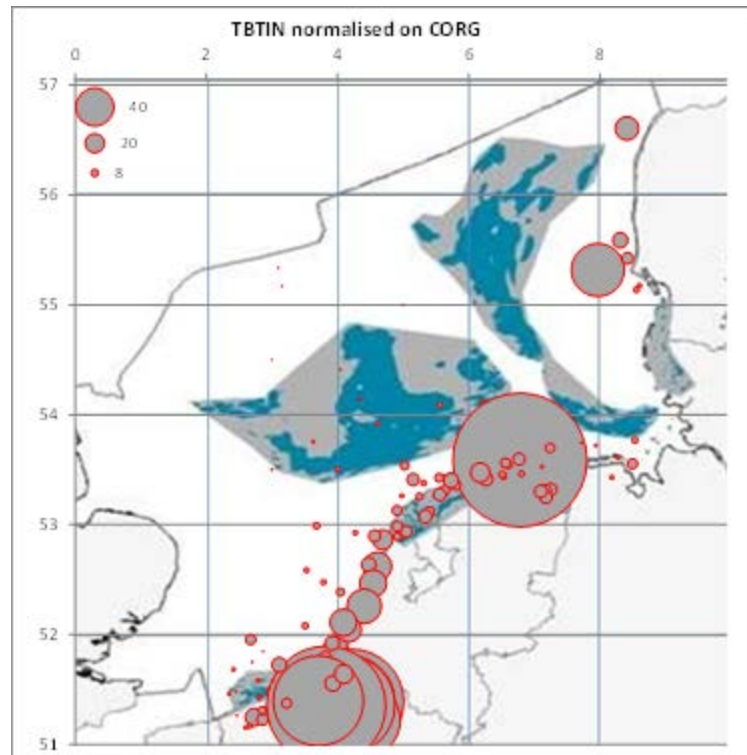


Figure 4.5. As Figure 4.3, but for tributyltin concentrations ($\mu\text{g/kg dw}$, normalised to 2.5% total organic carbon).

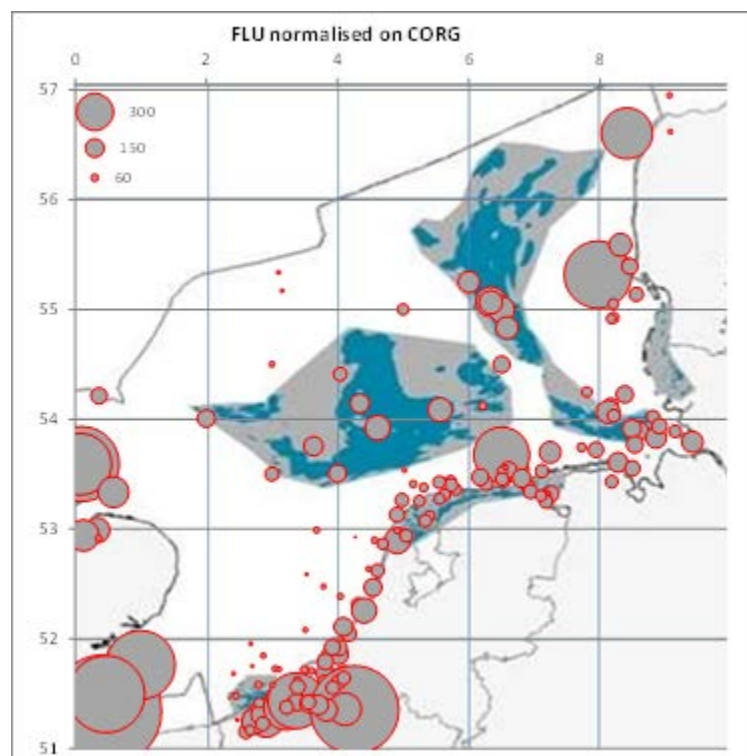


Figure 4.6. As Figure 4.3, but for fluoranthene ($\mu\text{g/kg dw}$, normalised to 2.5% total organic carbon).

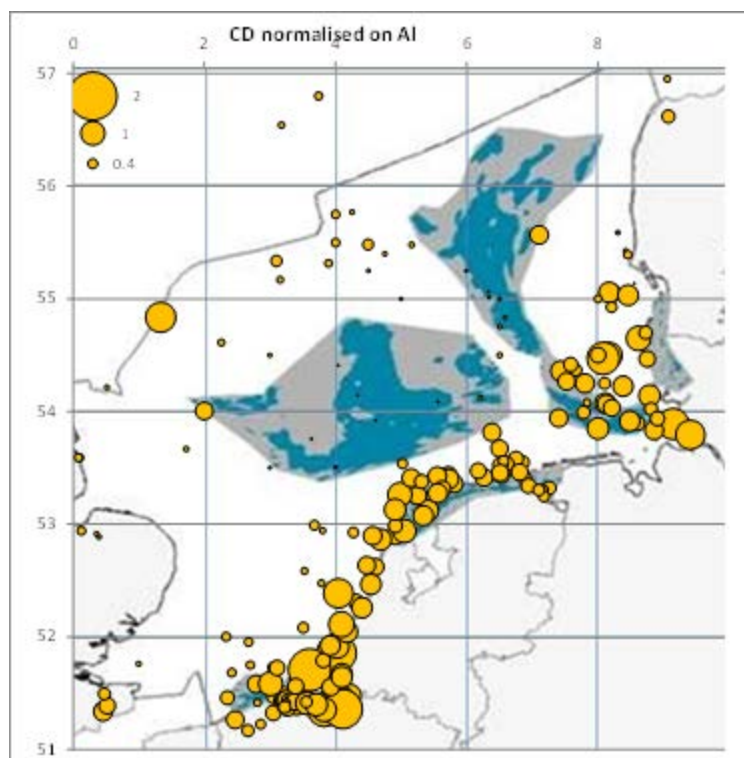


Figure 4.7. As Figure 4.3, but for cadmium concentrations (mg/kg dw, normalised to 5% Al).

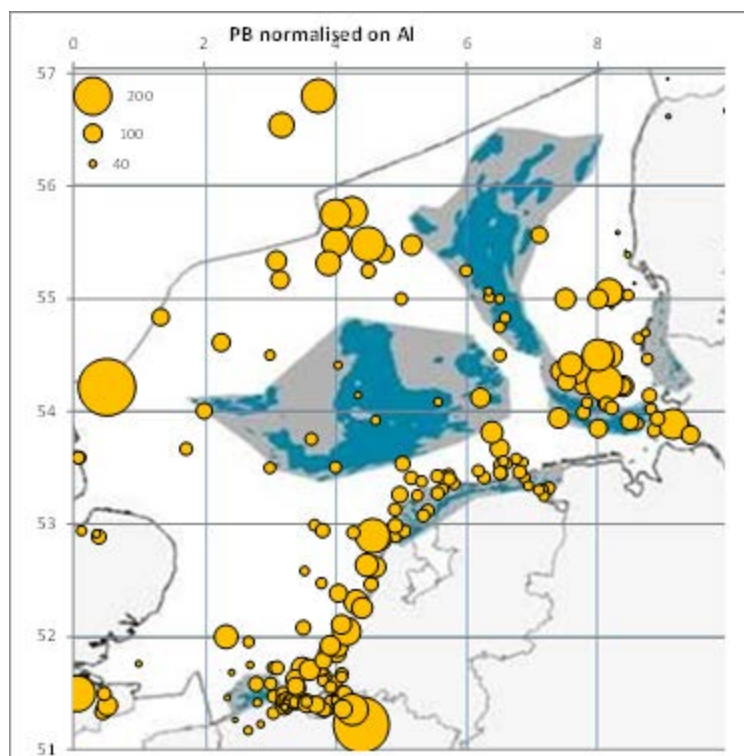


Figure 4.8. As Figure 4.3, but for lead concentrations (mg/kg dw, normalised to 5% Al).

The kriging approach described in Warren (1995, 1995) and cited in our ToR is a means to interpolate between sampling stations and investigate the distance from a station that the station is representative of. This is a geostatistical procedure that is now used within GIS-mapping software packages to interpolate between points

based on statistical relationships between those points and it can be used to provide a measure of uncertainty on the predictions. Due to time constraints, this question was addressed by a sub-group after the meeting.

Data from the 2013 OSPAR Working Group on Monitoring and on Trends and Effects of Substances in the Marine Environment (MIME) meeting were used to create semi-variograms and kriging data sets for the North Sea. The model mean for the last year was used as the value at each station (216 for Cd, 197 for Hg), and log transformed after converting to $\mu\text{g/kg}$ to avoid negative logarithms ($<1 \text{ mg/kg}$ concentrations).

The Kriging was performed using ArcGis product ArcMap 10.1, default setup for Empirical Bayesian Kriging (i.e. output cell size $4.5325\text{e-}2$, max 100 points in local model, circular search for neighbours with radius 437451 with 10-15 neighbours in 4 sectors). The Kriging procedure help file from ArcMap is available (<http://help.arcgis.com/en/arcgisdesktop/10.0/help/index.html#//003100000032000000>), but in short it averages neighbouring points to produce a grid for the whole area, in this case without borders (i.e. a point on each side of Jutland is averaged through Jutland). More advanced forms will respect borders (land) and only average with points not cut off by land, so this is a first attempt to see what it can bring to the table.

Semi-variograms depict the spatial autocorrelation of the measured sample points, allowing the relationship to be modelled. The distance where the model first flattens out is known as the range. Sample locations separated by distances closer than the range are spatially autocorrelated, whereas locations farther apart than the range are not (e.g. Figure 4.9).

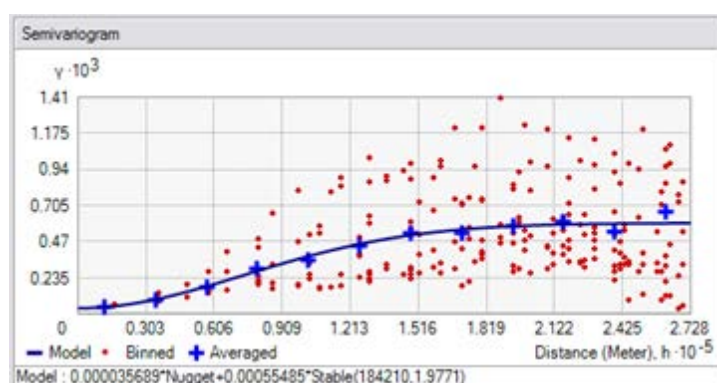


Figure 4.9. Example semi-variogram from the ArcMap help file, including the fitted model. Where the fitted line flattens the sampling sites are no longer auto-correlated.

For presentation, the scale for individual stations and the output of the Empirical Bayesian Kriging was divided into standard deviation groups of $-0.5 - 0.5$ standard deviations and steps of $+$ or $-$ one standard deviation from these. This results in “red” for results > 2.5 standard deviations, and yellow for the range around one standard deviation, green between $-1.5 - -0.5$ standard deviations and blue for < -1.5 standard deviations, the actual ranges are shown in Table 4.2 below.

Table 4.2. Scale ranges in concentration of log-transformed Cd and Hg mean last year data.

Std. dev.	Cd	kriging Cd	Hg	Kriging Hg
< -2.5			0.092 – 1.272	1.156
-2.5 – -1.5	1.846 – 2.021	1.156	1.272 – 1.698	
-1.5 – -0.5	2.021 – 2.402		1.698 – 2.125	
-0.5 – 0.5	2.402 – 2.783		2.125 – 2.552	
0.5 – 1.5	2.783 – 3.164		2.552 – 2.978	
1.5 – 2.5	3.164 – 3.545		2.978 – 3.405	
>2.5	3.545 – 3.963	3.1923	3.405 – 3.750	3.192

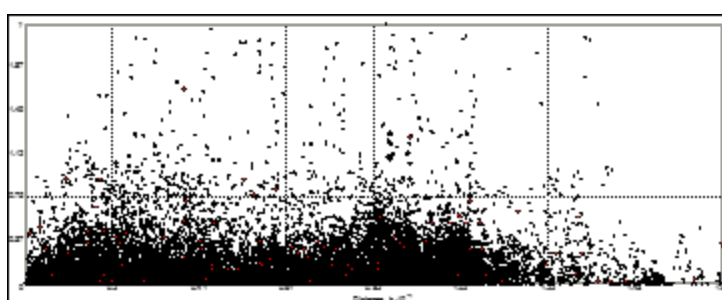


Figure 4.9. Cd logtransformed (log(1000*meanly)) – Semivariogram.

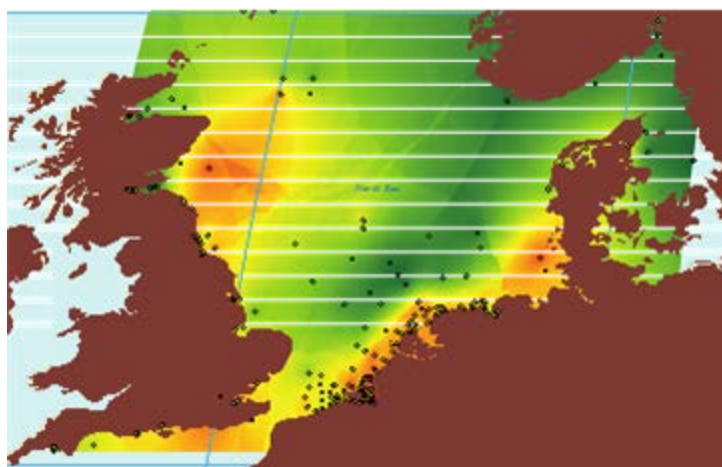


Figure 4.10. Results for Cadmium kriging of Cd. Notice the effect of two red points off Scotland and responsible for the whole red area off the Scottish coast.

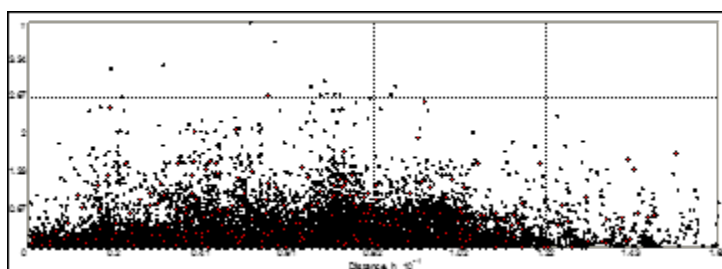


Figure 4.11. Hg logtransformed (log(1000*meanly)) – Semivariogram.

The dataset used directly did not yield sensible semivariograms, as it is controlled by a handful (Cd) or a bit more (Hg) high results, and therefore do not have any kind of increasing influence by distance (on the contrary).

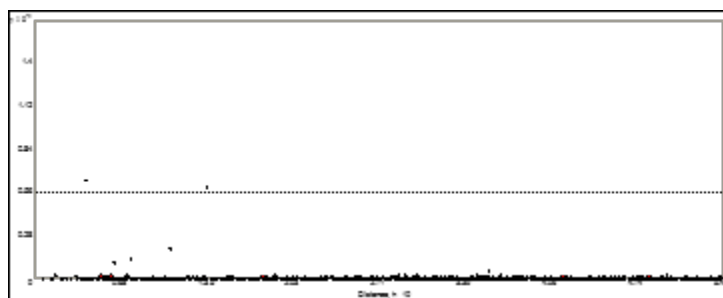


Figure 4.12. Cd semivariogram based on mean last year concentrations in mg/kg.

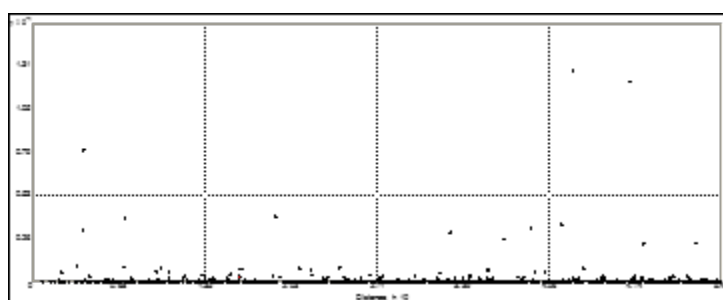


Figure 4.13. Hg semivariogram based on mean last year concentrations in mg/kg.

To summarise the answers to the questions we attempted to answer:

Q1: Can sediment transport models be used to inform on the required spatial distribution of sediment monitoring stations? Not at this point in time

Q2: Can we use existing monitoring stations to say whether we have GES? Yes, if they are in depositional areas; a power analysis is required to establish if more or fewer sites are required; the assessment of GES should be done on data expressed as whole sediment concentrations – this would require back-calculated for concentrations in the sieved fraction.

Q3: How does concentration variability relate to the size of a geographic area / strata? In general, larger areas have more variability, but there is not a simple relationship that can be used to quantify this. Furthermore, the degree of variability will differ for different substances and between regions.

Q4: Can we say how big a geographical area an individual sampling station represents? GIS-based kriging may offer the possibility to do this quantitatively, although the geographical area represented by any sampling station will be different for different substances. This can also be observed visually from simple bubble plots.

5 Special request to review and update Technical Annexes for determination of organotins and of metals in sediments

The 2014 meeting of WGMS was held in Copenhagen, concurrently with the annual meetings of the Marine Chemistry Working Group (MCWG), and the Working Group on Biological Effects of Contaminants (WGBEC). This allowed experts from the three groups to collaborate on this request, which was also on the MCWG ToR. The revision and update of the “Metals in Sediment” Technical Annex was undertaken jointly by WGMS and MCWG and is attached as Annex 5 to this report. The revision and update of the “Organotins in Sediment” Technical Annex was undertaken jointly by all three groups and is attached as Annex 6 to this report. The two Technical Annexes were submitted to ICES by the Chair of MCWG (Katrin Vorkamp) on 31 March 2014.

6 Multiannual Terms of Reference

WGMS will be moving to multiannual ToRs from 2015 and the 2014 meeting put a significant amount of thought and deliberation into these. At the 2013 meeting the Group considered that there was a continuing need for the group to exist and suggested some areas that it should work on. This position was reinforced during discussion at the 2014 and the multiannual ToRs presented in Annex 3 were developed.

7 Background concentrations

No new data were received during the meeting.

8 Passive sampling

As noted above, the 2014 meeting of WGMS was held concurrently with the annual meetings of the Marine Chemistry Working Group (MCWG), and the Working Group on Biological Effects of Contaminants (WGBEC). In order to build upon the work done last year by the ICES Workshop on the Application of Passive Sampling and Passive Dosing to Contaminants in Marine Media (WKPSPD 2013), a joint session on passive sampling was held between the three Working Groups. This was intended to result in information and knowledge exchange between the groups and to stimulate joint activities that would see this technique move forward with respect to being able to be used in environmental monitoring programmes. A key issue for that development is the availability of suitable assessment criteria, particularly EAC/EQS values (see 8.2 below).

8.1 Presentations during the WGMS / MCWG / WGBEC plenary session on passive sampling

Prof. Philip Mayer (Technical University of Denmark) was an invited speaker to the joint meeting of WGMS, WGMG and WGBEC and presented on the use of passive sampling of hydrophobic substances in environmental monitoring and on the use of passive dosing of hydrophobic contaminants in understanding mixture toxicity. Foppe Smedes (Deltares, NL; Recetox, CZ) presented on the use of passive sampling of hydrophobic contaminants in comparison to biota sampling for environmental monitoring and also showed sediment contaminant concentration data derived from passive sampling of sediments from the ICON project (International Workshop on

Integrated Assessment of Contaminant Impacts on the North Sea), with which several members of WGBEC were involved. Maria Belzunce (Azti-Technalia, SP) presented on the use of the Diffusive Gradients in Thin Films (DGT) technique for passive sampling of metals to explain differences in bioaccumulation occurring in identical sediment deployed in field and laboratory. Lutz Ahrens (University of Agricultural Sciences, SE) presented on the suitability of different passive samplers for the determination of WFD priority substances (especially pesticides and herbicides) in water. Abstracts of presentations are below.

Philipp Mayer: *Equilibrium sampling and passive dosing of hydrophobic pollutants – approaches, applications and findings*

Philipp Mayer presented research conducted by his group and others on equilibrium passive sampling of nonpolar contaminants, with a focus on sediments. This method allows to measure pore water concentrations of freely dissolved compounds (C_{free}) in the range $3 < \log K_{\text{OW}} < 8$ by incubating micrometer thin polymer coatings in sediments for periods of up to a few weeks. C_{free} is better related to sediment toxicity and bioaccumulation than total concentrations in the sediment phase, even if the latter are normalised to organic carbon. The concentration in the polymer phase (C_{polymer}) is also a good measure of the toxicity of these sediments. Using a polymer-lipid partition coefficient, C_{polymer} can easily be converted to an equilibrium concentration that a nonpolar lipid phase would have (C_{lipid}). Finally, this lipid based concentration can be directly compared with lipid normalised contaminant concentrations in biota. The latter concentrations are typically smaller than the passive sampler derived lipid concentrations.

Philipp Mayer further showed that equilibrium passive sampling allowed for identifying pollution sources and assessing the degree of sediment-water equilibrium in the environment, and that these data were easier to interpret than biota-sediment accumulation factors.

Below, some references are given for further reading.

References

- Jahnke A., Mayer, P., McLachlan, M.S. (2012). Sensitive Equilibrium Sampling to Study Polychlorinated Biphenyl Disposition in Baltic Sea Sediment. *Environmental Science and Technology* 46, 10114–10122.
- Jahnke, A., Mayer, P., McLachlan, M.S., Wickström, H., Gilbert, D., MacLeod, M. (2014). Silicone passive equilibrium samplers as ‘chemometers’ in eels and sediments of a Swedish lake. *Environmental Science: Processes & Impacts* 16, 464-472.
- Mäenpää, K., Leppänen, M.T., Reichenberg, F., Figueiredo, K., Mayer, P. (2011). Equilibrium sampling of persistent and bioaccumulative compounds in soil and sediment: comparison of two approaches to determine equilibrium partitioning concentrations in lipids. *Environmental Science and Technology* 45, 1041-1047.
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Witt, G., Lang, S.C., Ullmann, D., Schaffrath, G., Schmidt, K., Schulz-Bull, D., Mayer, P. (2013). A passive sampler for in situ measurements of freely dissolved concentrations of hydrophobic organic chemicals in sediments. *Environmental Science & Technology* 47, 7830-7839.

Foppe Smedes (WGMS/MCWG): *A comparison of lipid based concentrations of PCBs and PAHs obtained through passive sampling with lipid normalized concentrations in biota*

Foppe Smedes (DELTA RES, The Netherlands) illustrated the use of passive samplers for deriving equivalent lipid-based concentrations (C_{lipid}), which are for risk assessment easier to interpret than C_{free} , and allow for direct comparison with lipid-based concentrations in biota. He showed that different types of passive samplers yield the same values of C_{lipid} , indicating the robustness of this method. The work had been conducted in collaboration with Tatsiana P. Rusina and Philipp Mayer.

Foppe Smedes (WGMS/MCWG): *Passive sampling in sediments in and around the North Sea – ICES ICON project.*

Within the ICES ICON project silicone rubber passive samplers were exposed to 13 sediment samples taken from the Mediterranean to Iceland, including estuarine as well as open sea sediment. PAHs, PCBs, musk compounds, organo-phosphates, several organochlorine pesticides (including chlordanes), PBDEs and dioxins could be detected in samplers from virtually all locations. Higher concentrations were observed in estuaries for compounds that enter the marine environment through that route. Compounds that primarily enter the marine environment from diffuse sources, e.g. atmospheric deposition, showed concentrations much more equal for estuaries and open sea. For example chlordane, a pesticide not used in Europe, was present in open sea samples at the same levels as in estuaries. The results indicate that passive sampling allows very sensitive analyses of the contaminant levels in sediments. Furthermore, the same time and spatial comparison is possible as in conventional sampling, without the need for normalisation of the data for sediment characteristics. Foppe Smedes acknowledged contributions of Henry Beeltje (TNO-Utrecht, NL), Petr Kukucka (RECETOX, Brno, CZ) and Dick Vethaak (Deltares, Delft, NL).

Maria J Belzunce (WGMS) - *Utilising DGT-labile metal measurements to explain differences in bioaccumulation occurring in identical sediment deployed in field and laboratory.* Belzunce-Segarra, M.J., Simpson, S., Amato, E., Spadaro, D., Hamilton, I., Jarolimek, C., Jolley, D.

Maria Belzunce (AZTI-Tecnalia, Spain), presented a study with aims to: (a) investigate the metal bioavailability-organism response relationship utilising DGT techniques in sediments and metal accumulation in benthic bivalves, and (b) evaluate in which extent metal bioavailability and bioaccumulation measured *in situ* conditions are comparable with data obtained under laboratory conditions.

A field and laboratory based experiments were conducted simultaneously over 31 days. *In situ* deployment system was prepared with two stainless steel cages contain-

ing a range of metal contaminated marine sediments. The cages were submerged (0.5 m depth from the water surface) in Woronora estuary (Sydney, Australia). A total of 8 metal contaminated sediments (plus replicates) were prepared and placed into plastic beakers inside the cages. Seven individuals of the bivalve *Tellina deltoidea* of similar size (0.5-1.0 cm length) were added in each beaker. Under laboratory conditions clean and filtered sea water was used; the overlaying water was changed 2 times a week and the bivalves were feed 2 times a week. DGT-probes were deployed in each sediment twice during the test period, and overlying waters were also sampled throughout the laboratory test. At the end of the experiment the cages were retrieved from the field site and transported to the laboratory. For all treatments, sub-samples from three sediment depths were analysed for metals, organic carbon and AVS-SEM. The surviving bivalves were isolated, counted, and then allowed to depurate in clean seawater for 24 h, before being analysed for metal content.

Results show differences in metal concentration in sediments after 31 days deployment in field with respect sediments exposed in laboratory conditions that influence metal bioavailability. The DGT-metal flux measurements show differences in metal content in pore waters and in the overlaying water in the two scenarios (laboratory and field deployments) that explain the higher metal bioaccumulation obtained in the laboratory tested bivalves. DGT probes are useful tools that allow describing the relationships between the metal bioaccumulation by the bivalves and metal in the sediments and the various factors influencing metal bioavailability. This study was made in collaboration with the Centre for Environmental Contaminants Research (CSIRO, Sydney) and the School of Chemistry, University of Wollongong, NSW, Australia

Lutz Ahrens (MCWG): *Calibration and Field Evaluation of Passive Samplers for Monitoring Pesticides in Water*

Lutz Ahrens (SLU, Sweden) presented preliminary results on calibration and field evaluation of passive samplers for monitoring pesticides in water. The objectives of this study were i) to characterize six passive sampler types in a laboratory uptake study, ii) to apply three passive sampler types in two Swedish river systems, and iii) to compare passive sampling and active sampling. In this study, the passive samplers were characterized for about 150 individual pesticides including 20 priority substances of the EU Water Framework Directive (WFD). The passive sampler adsorbents included i) POCIS A: Pharmaceutical-POCIS, polar organic chemical integrative sampler (Oasis hydrophilic-lipophilic balance (HLB) sorbent), ii) POCIS B: Pesticide-POCIS, triphasic sorbent admixture (Isolute ENV+ and Ambersorb 1500) enclosed in a polyethersulphone membrane, iii) Chemcatcher® SDB-RPS: Styrene divinyl benzene Empore™ disk, iv) Chemcatcher® C18: Empore™ disk, v) silicone rubber (SR), and vi) low-density polyethylene (LDPE). Overall, passive sampling is a promising tool for monitoring of pesticides in water with minimal infrastructure and low contaminant concentrations. However, more research is needed to improve our understanding of the concept, challenges, and application of passive sampling for future monitoring strategies.

8.2 Review and discuss information on effects of freely dissolved concentrations, with a view of developing environmental assessment criteria, in a joint session with WGBEC and MCWG

It was noted that the discussion on the relevance of passive sampling methods for environmental risk assessment of contaminants is presently limited to nonpolar contaminants and metals.

WGMS recognises the relevance of these methods for the risk assessments of contaminated sediments. Some members feel, however, that sediment characteristics may also be important in this respect, therefore discussion within WGMS is ongoing.

WGBEC expressed interest to further look into the use of passive sampler based C_{free} as a proxy for toxicity for benthic and pelagic organisms and MCWG expressed interest to continue discussing the above issues with WGMS and WGBEC. The WGMS would welcome further interaction with WGBEC and MCWG in relation to its discussions regarding C_{free} and sediment properties in relation to toxicity. It was highlighted in the discussion that work on developing assessment criteria based on C_{free} was initiated by ICES WKPSPD, but that work to follow-up on the one-off workshop would have to be through MCWG, WGMS and WGBEC. In order to keep the momentum from the workshop, the three Working Groups agreed to work towards the long-term goal of developing environmental assessment criteria and agreed methodology (e.g. TIMES papers). To this end, WGMS agreed to establish a citation software database for recording information on studies relating toxicity to C_{free} (to help derive EACs). See also recommendations in section 12.

8.3 Review and discuss information on mixture toxicity derived from passive dosing, in a joint session with WGBEC and MCWG

As described in section 8.2, WGMS would welcome further interactions with MCWG and WGBEC on specific aspects of passive sampling/passive dosing. WGMS and MCWG felt that WGBEC could contribute significantly to the use of passive dosing techniques in developing criteria for assessing contaminant concentration data obtained from passive sampling, and for toxicity testing of contaminant mixtures. WGBEC agreed that they would be interested in these topics. WGMS agreed to develop a list of publications reporting passive sampling-derived toxicity data.

It was agreed between the three Working Groups that a recommendation (Section 12) would be given that describes WGMS's interest in contributions from WGBEC.

8.4 Review draft TIMES manuscript on determinations of sampler–water partitioning coefficients

A subgroup of members of WGMS and MCWG (Kees Booij, Foppe Smedes, Jacek Tronczynski, Katrin Vorkamp, Kine Bæk, Lutz Ahrens, Lynda Webster, Norbert Theobald, Celine Tixier, Ian Allan) outlined this draft during the meeting and agreed on the details of the methods that will be recommended. It is expected that a final draft can be produced intersessionally. Laboratories may be invited to test the recommended methods before finalising the manuscript, but it is recognised that laboratories may not be able to do this if funding is not available.

8.5 Review draft TIMES manuscript on passive sampling of sediments for hydrophobic contaminants

A draft manuscript on sediment passive sampling was produced by WGMS in 2007, with Foppe Smedes as the lead author. Time constraints at WGMS2014 prevented a review of this document, although it was recognised that it required further development and it is proposed to address this at WGMS 2014. WGMS members who are potential contributors to this document were identified as Ian Allen, Celine Tixier, Foppe Smedes and Craig Robinson, together with Kees Booij of MCWG; whilst all of these recognised the need for this work, it is unfortunate that none will have the capacity to undertake work on the document intersessionally.

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

No questions were received.

10 Marine Litter

The following is the agreed text from the joint MCWG/WGBEC/WGMS session on marine litter, see also <http://www.ices.dk/news-and-events/news-archive/news/Pages/43-scientists,-three-expert-groups,-one-overriding-theme.aspx>

The joint session was chaired by WGBEC who also provided the majority of presentations on marine litter and microplastics, whilst Marilyn Sørensen of the ICES Data Centre presented the Data Centre's work on a draft format for litter reporting.

Thomas Maes (WGBEC): Litter - the plastic tide

Thomas Maes (CEFAS, UK) presented a comprehensive review of several aspects of the marine litter issue. The presentation was structured along three subtitles:

- Thrashing the waves
- Marine litter and the MFSD
- CEFAS and EU marine litter work

1. Thrashing the waves

The term "Marine Litter" has been introduced to describe "any persistent, manufactured or processed solid material discarded, disposed of, or abandoned in the marine and coastal environment". It consists of articles that have been made or used by people and, subsequently, deliberately discarded or accidentally lost. They originate from ocean-based or land-based sources and can be found in marine environments around the globe. Most sources of marine pollution are land based. Marine litter, mainly plastic, poses a serious environmental threat to marine organisms, as well as a series of economical and social problems. The majority of marine debris is comprised of plastic materials (60–80% overall and 90% of floating debris).

All marine litter particles smaller than 5 mm are considered microparticles. Most microparticles consist out of microplastics, although other types exist. The abundance and global distribution of microplastics in the oceans has steadily increased over the decades to around the year 2000 following the rising plastic consumption worldwide since the 1940s. However, there has been a decrease in the average size of plastic litter over this time.

- Primary microplastics are produced either for direct use, such as for exfoliants, cosmetics, industrial abrasives or for indirect use as precursors (nurdles or virgin resin pellets) for the production of multiple plastic consumer products
- Secondary: Microplastics formed in the environment as a consequence of the breakdown of larger plastic material, especially marine debris, into smaller and smaller fragments (so called "secondary microplastics"). The breakdown is caused by mechanical forces (e.g. waves) and/or photochemical processes triggered by sunlight (especially UVB)
- Other types of microparticles:
 - Synthetic fibres shedding of textiles by domestic clothes washing
 - Rubber fragments from tires rubbing tarmac
 - Fly ash fine particles that rise with the flue gases after combustion
 - ...

The potential impacts of litter span both economic and ecological dimensions. The following section highlights the different aspects that are considered relevant.

- Economic
 - Losses to fishing and shipping industry
 - Clean up costs on beaches
 - Loss of tourist revenues
 - Aesthetic disturbance
- Ecological
 - Ingestion
 - Entanglement
 - Introduction of invasive species
 - Bioavailability and transfer due to sorbing/leaching
 - Smothering
 - Disturbance

Marine litter comes from a variety of land-based and sea-based sources and is essentially a consequence of poor waste management. However, the main sources can be grouped as follows:

The main land-based sources of marine litter

- Discharge of untreated municipal sewage, including storm water discharges and overflows
- Tourism (recreational visitors to the coast; beach-goers)
- Riverine transport of waste from landfills or other sources along rivers and other inland waterways and canals
- Industrial facilities: Solid waste from landfills, and untreated waste water
- Municipal landfills (waste dumps) located on the coast or inland
- Direct littering

The main sea/ocean-based sources of marine litter

- Fishing vessels
- Merchant shipping, ferries and cruise liners
- Military fleets and research vessels
- Pleasure craft

- Offshore oil and gas platforms
- Fish farming installations
- ...

2. Marine litter and the MSFD

The MSFD requires member states to manage their seas to achieve Good Environmental Status (GES) by 2020. MSFD Descriptor 10 requires litter to be at levels where the *'properties and quantities of marine litter do not cause harm to the coastal and marine environments'*.

MSFD criteria and indicators require understanding and monitoring of:

- The characteristics of litter in the marine and coastal environment – including:
 - Trends in the amount of litter washed ashore and/or deposited on coastlines, including analysis of its composition, spatial distribution and, where possible, source (10.1.1)
 - Trends in the amount of litter in the water column (including floating at the surface) and deposited on the sea-floor, including analysis of its composition, spatial distribution and, where possible, source (10.1.2)
 - Trends in the amount, distribution and, where possible, composition of micro-particles (in particular micro-plastics)
- The impacts of litter on marine life – trends in the amount and composition of litter ingested by marine animals.

3. CEFAS and EU marine litter work

CEFAS is involved in several national and international marine litter projects. Thomas Maes (Cefas) focused on two EU projects MICRO and MARLISCO:

- the EU Interreg 2 Seas MICRO:

The Micro EU Interreg project is monitoring microplastics (MP) within the 2 Seas Region and will provide a risk assessment based on field observations, lab experiments and mathematical models. MICRO is a cross border cooperation to prevent environmental, technological and human risks attributed to MP. Furthermore the project will contribute to establish common strategies for environmental risk assessment by modelling the potential impacts on the environment, and by proposing follow-up tools and mitigation measures. The three main pillars of the project are:

- Scientific: a risk assessment of the current situation by combining distribution data, modelling and biological effect measurements with socio economic endpoints.
- Educational/knowledge exchange: establishing good practices for adequate monitoring or impact determination across Europe.
- Public/scientific awareness: increase awareness of human behaviour in relation to waste production and management by creating co-responsibility among the different actors.

- the EU FP7 MARLISCO project:

MARLISCO activities take place in the **four European Regional Seas**: North-East Atlantic, Baltic, Mediterranean and Black Sea, by a consortium with members located in **15 coastal countries**. MARLISCO's overarching goal is to **raise public awareness, facilitate dialogue** and **promote co-responsibility** among the different actors towards a **joint vision** for the **sustainable management of marine litter across all European seas**. It will do this by developing innovative mechanisms and tools. MARLISCO aims to effectively **engage, inform** and **empower society**, reaching the widest possible audience. Its activities include:

- A **scoping study** of the sources and trends regarding marine litter in each Regional Sea.
- A collection of **best practices** from all partner countries.
- A **survey** on the prevailing perceptions and attitudes of different stakeholders regarding marine litter.
- A European **video contest** for youngsters to collect their visions on the issue of marine litter and empower them as agents of change in society.
- **National debates** in 12 partner countries.
- Diversified, tailor-made **national activities** including exhibitions, workshops, festivals, clean ups, etc.

Bavo de Witte (MCWG) and Lisa Devries (WGBEC): The role of microplastics and marine litter as a vector for chemical and microbial contamination

Bavo de Witte and Lisa Devries (both ILVO, Belgium) presented recent results of their research into the associations between litter and contaminants in terms of the following three presentations:

Marine litter as a vector for contamination

A quantitative GC-MS screening was performed on marine litter, present within benthos beam trawl nets during fishing activities. No clear indication of chemical contamination was found on blue synthetic rope. None of the OSPAR -7 indicator PCBs were found at concentrations > 0.1 ng/g. The origin of determined PAHs, alkylated PAHs, alkanes, alkenes and alkylated aromatic compounds may be pyrogenic/petrogenic pollution as well as plastic production. Phenols and specific antioxidants and UV-absorbers can also be related to plastic production.

Microplastics as a vector for PCBs

Little data is available on the role of microplastics as a vector for PCBs through the marine trophic levels and impact studies are required under controlled conditions. Benthic marine organisms such as the common shore crab and Norway lobster were exposed to PCB loaded microplastics under controlled laboratory conditions. In these experiments, 500-600 µm diameter polyethylene or polystyrene spheres were loaded with PCBs. The microspheres will pass the digestive tract without accumulation in the organism and egestion of the spheres was observed within two days after uptake. Within this research, it was shown that PCBs could desorb from the microspheres during the short period in the digestive system, but only a very small uptake of PCBs was observed by Norway lobster. No additional effect caused by the microspheres could be observed.

Plastic litter as a vector for bacteria

This work had been carried out by Lisa Devriese, Caroline de Tender and Sara Maes (all ILVO, Belgium). The possibility for microplastics and litter to act as a vector for bacteria and pathogens was suggested based on a bacterial screening on beach pellets, marine plastic litter and plastic beach litter. Diverse methods such as Next Generation Sequencing, TOPO TA cloning, PCR-DGGE were used to identify the bacterial communities of the different types of plastic.

Michiel Kotterman (MCWG): Microplastics as vectors of organic contaminants.

Presentation Plastic Research by Wageningen UR and IMARES UR Michiel Kotterman presented shortly the research on plastics. Next to monitoring the presence of plastics in the environment (as monitored by trawling; bottom and egg surveys), in biota (fish, Fulmars and seals) the main research topic is to determine the role of microplastics. Are they a vector of contaminants, enhancing the uptake of contaminants by biota, or are they a sink for some contaminants due to their high affinity for some contaminants, lowering the exposure.

This is being investigated with lugworms under realistic conditions, micro-PS in contaminated sediments (Besseling E.), and models for effects of plastic ingestions have been made (Koelmans B.). So far, plastics can be vector as well as sink, the effects under natural conditions are, from of risk assessment perspective, generally small. More data is required for proof and to improve the models. Therefore, research will be focussed on the net effects of plastic on the uptake of contaminants under natural conditions.

Within EU project ECSAFESEAFOOD IMARES is involved in feeding trials of fishes. Salmon will be exposed to plastics and contaminants in the feed. In one treatment plastics will be equilibrated with the contaminants before feeding, while in another treatment clean plastics will be added to contaminated food while feeding. This may add to the understanding of processes (rates especially) during the digestion.

Reference

Koelmans, A.A.; Besseling, E.; Foekema, E.M. (2014). Leaching of plastic additives to marine organisms. *Environ. Pollut.* 187, 49-54.

Jakob Strand (WGBEC): Relationship between microplastic particles, sediment characters and contaminants in sediments from Danish waters

Jakob Strand (Aarhus University, Denmark) gave a presentation on the relationships between microplastic particles, sediment characteristics and contaminants in sediments from Danish waters based on a study on distribution of microplastic particles (38 µm – 5mm) in sediment in the Danish waters from the Baltic Sea towards the North Sea. The results indicate that normalisation of microplastic abundances to adequate sediment characters can reduce the variability caused by natural heterogeneity between samples and thereby increase the power of identifying more or less affected areas. Strong relationships between the content of microplastics in sediments and both %TOC and fine sediment fraction (<63 µm) were found throughout the area supporting that microplastics will accumulate in sedimentary depositional areas – i.e. with parallels to organic pollutants sorbed to organic materials. Positive correlations were also established to contaminants, especially PAHs and to lesser extent to al-

kylphenols and phthalates in sediments. It could be due to co-variation with sources and TOC rather than due to chemical extraction of microplastic particles. However, at least antifouling agents like TBT in paint flakes from ship lanes and harbours can be one exception.

Bjørn Einar Grøsvik (WGBEC): Monitoring marine litter, a part of the joint Norwegian/Russian ecosystem survey in the Barents Sea

Bjørn Einar Grøsvik (IMR, Norway) presented a collaboration project with the Polar Research Institute of Marine Fisheries and Oceanography (PINRO) in Russia. Co-workers on this study were Elena Eriksen (IMR, Norway) and Tatiana Prokhorova and Pavel Krivosheya (both PINRO, Russia). Since 2004 these institutes have collaborated on ecosystem based surveys in the Barents Sea. From 2010 registration of marine litter has been a part of this collaboration.

Surface investigations and trawl catches have demonstrated highest occurrence of litter in the areas of intensive fishery and navigation. Plastic prevailed among observed litter. The main plastic concentration in the surveyed area was observed between 69° and 74°N and between 25° and 45°E, an area being under the influence of the Atlantic and coastal currents. Plastic might be brought further northwards and eastwards by the Novaya Zemlya and Kolguev-Pechora Currents. Floating timbers were observed in all investigated areas. Litter was observed in bottom trawls more frequently than in pelagic trawls. Other types of litter (metal, paper, rubber, textile, glass) were sporadically observed.

Marilynn Sørensen (ICES datacentre) gave a presentation on the requirements / developments for litter data recording at ICES

The ICES data centre has set up new litter record to include litter information in Environmental Reporting Format 3.2. In the framework of the MSFD (descriptor 10) the task group marine litter at the ICES Data Centre defined different litter categories in 2013. It was, however, too complex, to include the variability of types and sizes within the existing framework, and it was decided to set up a separate litter record. This includes the following information: depths min/max, litter size, litter reference list, parameters/unit/value, litter source, litter use, number of entangled biota, state of litter, polymer type, attached organisms (non-microbial). ERF3.2.5 is available on the MCWG SharePoint and comments to the new record can be given to marilynn.sorensen@ices.dk by the 1 April 2014.

It was suggested that one person of each group should give suggestions and that the database should be kept as lean as possible since this will lead to more people who will fill in the database. The rule-of-thumb is to only include parameters that are really essential for an assessment

11 Miscellaneous

11.1 QUASIMEME

Steven Tito gave a presentation on QUASIMEME during a joint session of WGMS and MCWG. One of the issues that came up after his presentation was related to the units for the metals analysis. WGMS agrees that for the new metals mg/kg would be the best unit, but most people are not intending to send data on these new determinants.

WGMS also recommends QUASIMEME to check the real levels of the determinants in the samples sent to participants for the intercalibration exercises, in order to assure that they are not under detection/quantification limits and so increase the likelihood of obtaining assigned values.

WGMS also encourages QUASIMEME to widely advertise the Passive Sampling intercalibration exercise. It was evident during the WGMS meeting that, although the information was in the present QUASIMEME brochure, many of the potential participants (who were present at the meeting) were not aware of the exercise.

WGMS further recognises that there can be an interest in a similar QUASIMEME exercise focusing on DGT and its use for the determination of trace metal elements as this technique is presently used by an increasing number of laboratories, including also those oriented to the analysis of soils or freshwater sediments. The biannual conference on DGT could be an excellent place to advertise such an exercise.

11.2 Assessment criteria for sediments

During the discussions on passive sampling, there was a desire from members of all three Working Groups (WGMS, MCWG and WGBEC) for further development of upper assessment criteria (e.g. EACs/EQs) for marine sediments that are related to sediment physicochemical characteristics. WGMS agreed to establish a citation software (e.g. Endnote) database to hold information on publications of sediment-based toxicity tests that include a description of the physicochemical characteristics.

12 Recommendations and action list

- 1) WGMS recommends that OSPAR updates the JAMP Guidelines for Monitoring Contaminants in Sediments following the revision undertaken at the joint meeting of WGMS and MCWG.
- 2) WGMS recommends that OSPAR considers including concentration data from sieved samples in sediment sampling designs for assessing for Good Environmental Status (c.f. ICES 2013 advice) and includes it in their revision of the JAMP Guidelines of Monitoring Contaminants in Sediments.
- 3) WGMS recommends that the requested “spatial monitoring guidelines” should be referred to as “guidelines for a region-scale monitoring programme.”
- 4) WGMS recommends that OSPAR MIME forwards our comments regarding the QUASIMEME proficiency testing scheme to the QUASIMEME Scientific Advisory Board.
- 5) WGMS recommends that WGBEC coordinates with WGMS in order to develop a database of publications concerning sediment toxicity, particularly with

data related to sediment physiochemical characteristics, to make these data available for the further development of sediment assessment criteria, e.g. for normalised sediment data.

- 6) WGMS recommends that WGBEC coordinates with WGMS in order to develop database of publications concerning toxicity of contaminants based on freely dissolved concentrations in order to make these data available for the further development of assessment criteria for use with passive sampling of sediments and water.
- 7) WGMS recommends that MCWG experts work with those of WGMS on further revision and development of guidelines for passive sampling of sediments.

13 Chair(s) for 2014

Lucía Viñas (Spain) stood down as co-chair and in her place Céline Tixier (France) was elected as co-chair. Post-meeting Céline has accepted the position, having received authority from her institute to do so.

14 Date and venue of next meeting

Assuming the new 3-year ToRs are accepted, WGMS will next meet from 2 to 6 March 2015, in Koblenz, Germany.

15 Closure of meeting

The meeting was closed at 1 p.m. on 7 March 2014.

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 Lucía Viñas, Spain and Craig Robinson, UK - Copenhagen, Denmark, 3-7 March 2014:

1. Opening of the meeting
2. Adoption of the agenda
3. Sediments monitoring
 - a. Finalize 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 2013 meeting of OSPAR/MIME in matters concerning sediments.
4. Background concentrations
 - a. Continue collection of data and develop background concentrations for alkylated PAHs and dioxins.
5. Passive Sampling
 - a. Initiate a review on the use of passive sampling for measurements in sediments in relation to assessing the state of the marine environment;
 - b. To report on on-going and new projects involving passive sampling.
 - c. To work on developing guidelines for the determination of passive sampler water partition coefficients
 - d. To work on the development of guidelines for passive sampling of sediments
6. Miscellaneous
 - a. Provide expert knowledge and guidance to ICES Data Centre (possibly via subgroup) as requested.

Annex 3: WGMS Multiannual terms of reference

The **Working Group on Marine Sediment** (WGMS), chaired by Craig Robinson (UK) and Celine Tixier (France), will meet in Koblenz, Germany, from the 2nd to the 6th of March 2015, to work on ToRs and generate deliverables as listed in the Table below.

WGMS will report on the activities of 2015 (Year 1) by 30 April 2015 to SSGHIE.

ToR descriptors

ToR	Description	Background	Science Plan topics addressed	Duration	Expected Deliverables
1	Respond to requests for advice from Regional Seas Conventions (e.g. OSPAR, EU) as required.		4.1, 4.2	3 years	Requested advice
2	Passive sampling (PS) in sediment				
	1a - Review of existing methods dealing with PS in sediment	Follow-up on the work of WKPSPD	4.1, 4.2	Year 1	Recommendation based on current status
	1b – Complete Guidelines for monitoring with PS in sediments for hydrophobic organic contaminants / produce guidelines for PS of metals	Guidelines required for technique to be acceptable for monitoring purposes.		3 years	Working with MCWG experts, produce TIMES paper(s) on the use of PS in sediments
	1c - To improve the understanding of the relation between data obtained by passive sampling in sediment and environmental quality (biota data, toxicity data, EACs)	Assessment criteria suitable to assess GES in sediments are lacking / require improvement. WGMS will work with WGBEC to attempt to close this knowledge gap		3 years	Dataset and advice to OSPAR on progress as passive sampling, which ICES WKPSPD have recommended the approach go on the pre-CEMP.
	1d- To review on-going or future projects with PS			Each year	Report to ICES

2	To explore the suitability / possibility of modelling to explain spatial distribution patterns of contaminants in sediment and inform on sources and hence possible MSFD measures	TEXT NEEDED.	4.1, 4.2	3 years	Report to OSPAR via ICES
3	Deep sea sediment monitoring To provide advice on sediment monitoring in the wider oceans as required for MSFD	Monitoring of the deep sea is required for the MSFD. Technically this is more difficult than for shallow seas and advice should be developed	4.1, 4.2	3 years	Advice to OSPAR via ICES on deep sea sediment monitoring
4	Impact of renewable energy devices (e.g. wind mill,...) To explore the potential risk impact in terms of release of contaminants (corrosion, anti-corrosion agents...)	Many hundreds of renewable energy devices are being placed in the marine environment. Resultant changes in hydrodynamics may release sediment-bound contaminants, there may be inputs of contaminants from their installation, operation and decommissioning.	4.2	3 years	Report to ICES and if necessary recommendations
5	Emerging issues: To assess the relevance and the potential risk impact of these issues Follow up of outcomes of other expert groups - Microplastics in sediment - Deep sea mining	Microplastics are of emerging concern and may be a vector for contaminant transfer to sediments, or from sediments to biota Mineral mining is a likely future source of anthropogenic disturbance to the deep sea and could result in the release of contaminants into otherwise relatively pristine environments	4.1, 4.2	3 years	Report to ICES Develop links up to relevant expert groups on marine litter Link-up with WGEXT who have a ToR to report to produce a summary paper concerning deep sea mining (What is being mined, where this is occurring, techniques being developed etc).

Summary of the Work Plan

Year 1	Complete review of techniques for passive sampling of marine sediments. Progress work towards completion of the remaining ToRs
Year 2	Progress work towards completion of the remaining ToRs
Year 3	Report on ToRs 2-5

Supporting information

Priority	This Group handles key issues regarding monitoring and assessment of contaminants in sediments. The current activities of this Group will lead ICES into issues related to the understanding of the relationship between human activities and marine ecosystems (estimation of pressure and impact, ...). Consequently, these activities are considered to have a high priority.
Resource requirements	The research programmes which provide the main input to this group are already underway, and resources are already committed. The additional resource required to undertake additional activities in the framework of this group is negligible.
Participants	The Group is normally attended by some 15-20 members and guests.
Secretariat facilities	None.
Financial	No financial implications.
Linkages to ACOM and groups under ACOM	There are no obvious direct linkages.
Linkages to other committees or groups	There are close working relationships with Marine Chemistry Working Group (MCWG) and Working Group on Biological Effects of Contaminants (WGBEC); some members of WGMS are also members of these. The work of WGMS is also relevant to the Working Group on the Effects of Extraction of Marine Sediments on the Marine Ecosystem (WGEXT).
Linkages to other organizations	OSPAR, HELCOM, MEDPOL, EU/JRC Expert Network on Contaminants

Annex 4: View of the ICES 2013 advice “Spatial design of a regional monitoring programme for contaminants in sediments” by the Netherlands

A design for a regional monitoring programme for contaminants in sediments has been developed in the ICES Working Group on Marine Sediments (WGMS)¹ in response to an OSPAR request² and lead to the ICES advice³ discussed here.

The objective of the design was to assess GES at a large (sub-)regional from data that could be analysed in a coherent and transparent way, without the need for ad-hoc ‘patching’ together of data collected in different ways for different purposes. The advantages were considered outweighing the disadvantages of having to change national monitoring programmes once every six years.

The developed design included the following steps

- 1) Identify areas of sediment with $\geq 20\%$ fines.
- 2) Create sampling strata (regions) containing only areas with $\geq 20\%$ fines.
- 3) Use existing data to estimate mean concentrations and variability in the sampling strata.
- 4) Undertake a power analysis to determine the number of samples required in each stratum to achieve a target uncertainty in the estimated mean concentrations.
- 5) Aggregate individual stratum assessments to the regional scale, by using the weighted mean of the individual stratum means, using stratum area as the weighting factor.
- 6) Refine the design in the light of the additional data obtained above (e.g. the location of strata, and the number of samples required per strata).
- 7) Statistically compare the aggregated values with the assessment criteria to determine compliance with GES.

The core of the design is the analysis of a sufficient number of samples collected from a defined region to demonstrate statistically that the criteria for good environmental status are met (EACs, ERL). A power analysis using the variability from existing data was used to estimate the number of samples required to achieve this. Data from the first monitoring occasion using the above design would be analysed to improve understanding of the variance in field data and to refine the number of samples required for the next round.

The regional monitoring concerns data from whole sediment samples, without any normalisation or correction grain size differences, on the grounds that the quality criteria (EACs, ERL) are also expressed on a whole sediment basis, not taking variation in the nature of the sediment into account. Concentration in whole sediment from sandy areas will generally be very low and consequently the guidelines suggest that only muddy samples (i.e. where the content of fines ($< 63\mu\text{m}$) is larger than 20%) should be analysed.

Discussion

The application of this protocol, and its refinement and possible future adaptation may benefit from some additional review in the light of emerging technical issues, weaknesses and interpretative perspectives.

Choice of concentrations of contaminants in whole sediment (no normalisation)

Normalisation is applied as a pragmatic approach to reduce variations caused by differences in bulk sediment properties, such as grain size, or organic carbon content. Measured concentrations are best used as comparative indicators of sediment quality if they are expressed on a similar matrix, e.g. the ratio between concentration and uptake capacity. This has always been the basis for developed normalisation procedures for trend monitoring of sediment quality, as reflected in ICES and OSPAR Guidelines for temporal trend monitoring⁴. The Guidelines also refer to comparison of field concentrations with assessment criteria. ICES guidelines refer to OSPAR EACs and ERLs given for whole sediment, but in the MSFD documents for Descriptor 8⁵ both EACs on normalized sediment compositions as well as ERLs on whole sediment are listed. Clearly, quality criteria for sediment which do not specify the bulk sediment composition are not really in agreement with the best current scientific understanding. Differences in bulk sediment composition will lead to differences in contaminant concentrations in sediment that will not necessarily be reflected in contaminant concentrations in water or organisms. There is awareness that expressing EAC/ERL on a total sediment basis, and testing GES on total sediment analyses is not the ideal way. ICES advice is given in the understanding that currently a better approach is lacking. ICES suggestions for a better approach pointing to the application of passive sampling which can, through a single matrix (the sampler), bridge different areas and environmental compartments, and quality criteria.

Strata with fines content >20%

Choosing only stations/samples with a with fines content >20% implies a certain degree of normalisation. Assuming that sediments with 80% fines will be rare, a maximum variation in composition can only comprise a factor 4. This approach however limits assessments to muddy areas which are rather rare in the southern North Sea, except very close to the coast and in estuaries, where the sediments reflect the inputs for most contaminants. To base regional monitoring primarily on coastal and estuarine areas requires the assumption that areas further offshore will meet GES if the areas close to the coast do so. Except for sea-born contaminants (burning waste on Sea, atmospheric and contamination from shipping) this assumption seems valid.

It is obviously very difficult to define clear directions or criteria on how sampling strata should be defined. The guidelines provide little advice, other than to use expert knowledge on coherence. Probably a new stratum should start if the differences in space becomes larger than differences in time; a criterion that is very difficult to verify due to the large variability arising in monitoring data using whole sediment samples. It is however clear that upward and downward trends should not occur within the same stratum.

Sampling and station issues

Within strata, simple random sampling should be applied to certify sound statistical distribution but this may conflict with selecting areas with a $\geq 20\%$ fine fraction. In spite of careful defining such strata actual taken samples or a number of them may not meet the criteria of $\geq 20\%$ fine fraction. The ICES advice does not mention what to

do in such cases but the WGMS2013 report suggests discarding these samples and perform re-sampling until a sufficient number of appropriate samples is reached. It is not clear whether this will always be an effective approach, especially if a new sampling cruise would be required for the additional samples. An alternative, more cost effective solution could be to remove sufficient coarse sand from samples not meeting the criterion, or restrict the random sampling to areas with known high content of fine material. This may in many cases approach the present distribution of fixed sampling stations in use for trend monitoring which are selected in sedimentation areas when possible. However the number of trend stations may not always be sufficient to cover the statistical requirements for the regional monitoring.

Case studies

Case studies play an important role in designing of the regional monitoring programme for contaminants in sediments. They give a basis for the indicating the number of samples required through the power analysis using the variability. The results were compared with EAC or ERL, whichever was higher. The GIS presentation shows the presence of areas with contents >20% fines in the southern North Sea and the case study generally provides confirmation. However it should be noted that a quite considerable amount of data in Table 1.5.6.8.1 (ICES Advice)³ was recalculated from actual measurements in the fraction <63µm (Oyster grounds and Wadden Sea, not sure about other areas?). Figure 1 below shows that measured fraction of fines in real samples from the Dutch part of the North Sea only rarely exceeds the 20%. So, if samples with the appropriate content of fines were not found in several past monitoring rounds it may require numerous samplings to obtain the required number of samples for the regional assessment. Using concentrations recalculated from the <63 µm fraction (multiply by 0.3) also may have biased the power analysis as the variability will not represent the true variation in whole sediment samples. Clearly, all these issues can be refined after a first try-out, but it indicates that the application of the guidelines is not as straightforward as implied by the ICES advice.

Situation regarding regional monitoring for The Netherlands

In the area monitored by the Netherlands, sediment with a fines content >20% is not found in the open sea and only occasionally occur in coastal and estuarine areas (Figure 1). Figure 1 shows where the content of fines (<63 µm) determined in whole sediment samples is, respectively, below 10, 20, and above 20%. Strict application of the guidelines would mean that only the Western Scheldt and the Wadden Sea areas qualify for applying regional monitoring, but they are not part of the MSFD. Such incomplete coverage of the Dutch monitoring area seems of limited value for the overall OSPAR monitoring and will likely not satisfy MSFD demands.

Following the spirit of the ICES advice, but not the letter, a qualitatively equal (or better) assessment for regions defined in the Dutch monitoring area can easily be performed within the present programme as this was designed to cover both trend and spatial monitoring using the same methods for different purposes so does not have problems that the above design intend to avoid. The sediment monitoring program of The Netherlands is quite dense and appropriate defined strata likely will contain sufficient sample points to perform the assessment as suggested, certainly when data from different years are combined. The above means that the same sampling sites, as presently established for the temporal and spatial trend monitoring programme, can also be used for the MSFD assessments. The guidelines would require whole samples with $\geq 20\%$ content of fines. Consequently, converting the data measured in the fine

fraction $<63\ \mu\text{m}$ to a hypothetical whole sample with 25% of fines provides data well within the range required in the guidelines. The level of 25% is similar to the average fines content over all sediment samples including the freshwater program. From an environmental perspective, the approach above is equally as sound as that proposed in the ICES advice, probably giving slightly less variable data. It further does not require the strict focus on areas in the strata containing the rather high content of fine grained sediment that may not be easy to find. The lower variability may allow a reduced number of samples to be analysed while retaining the same overall uncertainty in the mean value.

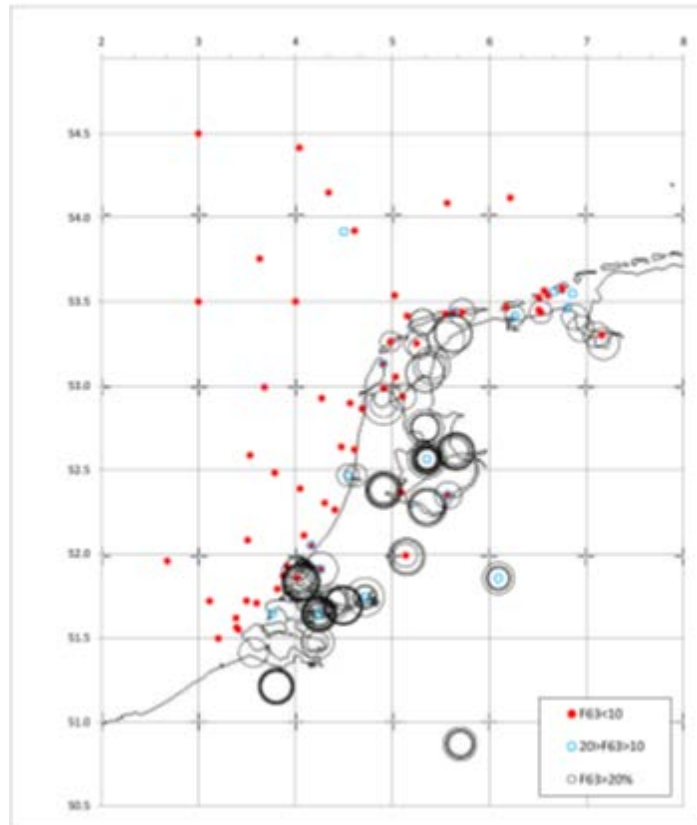


Figure 1. Map of Dutch monitoring stations indicating whether the content of fines, $<63\ \mu\text{m}$, is less than 10% (●), between 10 and 20% (○) or larger than 20% (○) (data retrieved from waterbase).

Random sampling is statistically advisable in order to represent the whole area of the strata. As outlined above, the chances of failing to sample sediments with $>20\%$ fines at the designated locations will strongly limit the added value over stationary sampling points. More or less fixed stations, provided they are well dispersed, can serve the same purpose. The highly dynamic nature of sediment in the southern North Sea suggests that sampling performed on the same place will be a “by nature” randomised sample.

It is unlikely that preventing the sample composition from varying over a factor 4 through using sieved fractions, and not randomising the sampling sites, will severely degrade the quality of a spatial design for regional monitoring. If randomisation is an absolute statistical necessity this could partly be applied in future assuring the historical trends are not lost. The “randomization” aspects will then only apply in varying around the nominal station coordinates within an area not larger than e.g. 10% the distance to adjacent locations. This is a sound compromise, leaning towards the ICES

advice while at the same will not be affecting the usefulness of the data for the established trend monitoring programme. A trial with existing data will reveal if this slightly amended application of the ICES advice on regional monitoring of contaminants in sediment is feasible and effective. This approach may be particularly appropriate considering that it seems to be a reasonable assumption that the present guidelines are an interim approach that may in future be replaced by passive sampling when procedures and assessment criteria for such methods are established^{3,6}.

References

- ¹ Report of the Working Group on Marine Sediments in Relation to pollution, March 2013, Lowesoft, UK. http://ices.dk/sites/pub/Publication_Reports/Expert_Group_Report/SSGHIE/2013/WGMS13.pdf
- ² OSPAR, request (OSPAR 2011/2)
- ³ ICES, Ecoregion subject, 1.5.6.8, Special request, Advice October 2013
- ⁴ JAMP Monitoring Guidelines. OSPAR Commission 2003, http://www.ospar.org/content/content.asp?menu=00900301400135_000000_000000.
- ⁵ MSFD Task Group 8 Report, Contaminants and Pollution Effects, Joint Report of JRC and ICES 2010, <http://ec.europa.eu/environment/marine/pdf/7-Task-Group-8.pdf>
- ⁶ Report of the Workshop on the Application of Passive Sampling and Passive Dosing to Contaminants in Marine Media (WKPSPD). ICES Workshop Report 2013, <http://ices.dk/sites/pub/Publication%20Reports/Expert%20Group%20Report/SSGHIE/2013/WKPSPD13.pdf>

Annex 5: OSPAR Technical Annex 6: Determination of metals in sediments – analytical methods

1. Introduction

This technical annex provides advice on the determination of metals (including metalloids and some non-metals like Se) in whole sediment and in sieved fractions. Determinations of trace metals can be achieved by acid digestion of the sediment followed by analysis of the digest solution by spectroscopic or spectrometric methods, or non-destructive techniques such as X-ray fluorescence analysis (XRF), instrumental neutron activation analysis (INAA) etc. The guidelines are intended to assist analytical chemists both in starting up metal analyses in sediments, and to those already performing such analyses. They do not provide full details on specific laboratory procedures. Further guidance may be sought from specialised laboratories and publications (e.g. Loring and Rantala, 1991; Popek, 2003) or general guidance for selection of analytical methods (e.g. Larsen *et al.*, 2011). Analyses should be carried out by experienced staff and the procedure should be validated.

Trace metals may occur in both fine and sand fractions of sediments. However, most natural and anthropogenic substances (metals and organic contaminants) show a much higher affinity to fine particulate matter than the coarse fraction. Iron and manganese oxy-hydroxide coatings, and constituents such as organic matter and clay minerals, contribute to the affinity for contaminants for this fine material.

Total methods, such as procedures involving total dissolution of sediment samples with hydrofluoric acid (HF) prior to analysis, or non-destructive methods without digestion such as neutron activation analysis (INAA) and X-ray fluorescence analysis, determine total trace metal contents in the whole sediment sample. In contrast, methods using a partial digestion with only strong acids, e.g. nitric acid or *aqua regia*, mainly measure trace metals in the fine fraction, and only extract small amounts of trace metals from the coarse fraction. For fine material, similar results have been obtained using both total and strong partial methods (Smedes *et al.*, 2000; QUASH/QUASIMEME intercalibrations).

2. Sampling, pre-treatment and storage

Sampling sediments for metals analysis should preferably be done using cleaned plastic equipment, but this may not always be possible (e.g. at sea). Where metal sampling gear such as grabs must be used, care must be taken to avoid contamination of the sample, for instance by sub-sampling only sediment that has had no contact with the walls of the sampling device (maintain at least 1 cm distance from sides). Sample thickness should be chosen according to the monitoring proposes.

For ordinary surveys, the upper 2 cm of the sediment are sampled, but for other purposes like retrospective surveys, core samples can be taken. If knowledge exists about the sedimentation rate, the sampling strategy can be based on this (e.g. Wadden Sea sampling of the upper 1 mm).

Sediments can be stored in closed plastic or glass containers. Samples must be sieved to 2 mm after sampling to remove large debris as well as large detritus and benthic organisms. Otherwise during further sample handling like storage, freezing or ultrasonic treatment, biotic material will deteriorate and become part of the sediment sample. Samples may then be further wet sieved to a smaller size fraction. Further

details on sieving procedures are available in the Technical Annex 5: Normalisation of Contaminant Concentrations in Sediments.

For total analysis, metals are usually not very sensitive with regard to storage conditions, so other measured parameters may determine how to store the samples. For total analysis of metals the sample can be stored at 4°C for a few weeks and for extended periods when frozen at -20°C, although direct wet sieving is preferred. For prolonged storage freeze-drying of samples can be considered. In this case contamination and losses of contaminants during freeze-drying have to be checked, in particular for volatile parameters (e.g. volatile organics) to be analysed in the same samples. Air-drying is not appropriate due to high contamination risks. Besides, samples may be difficult to disaggregate and mineral structures may be affected.

Once sieved and dried, samples should be homogenised and ground to a fine powder in a non-contaminating mill (e.g. made of agate or silicon nitride), and stored in plastic or glass containers until analysis.

3. Blanks and contamination

Any contact between the samples and metals should be avoided. If metallic implements are required during sampling (e.g. grab jaws), they should be of stainless steel and contact between the sub-sample and metal should be minimised.

Plastic and glassware should be cleaned using a laboratory washing machine incorporating an acid wash, or by an equivalent cleaning procedure. Some plastic ware may not need to be cleaned before first use for metals work, but this feature must be thoroughly examined (e.g. using acid leaching tests) before proceeding with any real samples.

Blanks should be taken through the whole procedure. In practice, this will generally represent the time from acid addition to a sample container through to the final measurement. There should be at least one analytical blank in a batch of 10-20 samples, representing 5–10% of the sample number.

For core-samples, care should be taken not to contaminate lower samples with upper samples in the process of cutting up the sediment core.

4. Digestion

4.1 Hydrofluoric acid digestion

HF digestions should be performed in polytetrafluorethylene (PTFE or PFA) vessels or equal quality, since the vessel must be metal-free and resist attack by the acid itself. Dried samples (normally 0.2-1g) should be accurately weighed into the vessel. Under fume extraction, the acid(s) are added. Some workers add HF first and leave the mixture to stand overnight, others add HF, nitric acid or *aqua regia* (see below); others use a perchloric acid mixture etc. In general, the mixtures are left to stand for a certain period of time (1 hour – overnight) to avoid problems with violent reactions, which may be prompted by the presence of organic matter in the sediment. Note that perchloric acid and organic matter can promote an explosive reaction, so this acid must be handled with great caution if applied to sediments. Specially designed fume hoods should be used for HF and perchloric acid treatments.

HF is corrosive and toxic. It is therefore necessary to either remove the acid or render it less harmful to the measurement instruments. The acid may either be boiled off,

which requires specialised facilities to extract the toxic fumes, or neutralised with boric acid (H_3BO_3), which is toxic itself.

Samples may be digested in a programmable heating block, with HF removal by evaporation. Alternatively, microwave digestions provide a rapid way to digest sediments. Some systems may allow the evaporation of HF, but in general microwaves use closed systems which allow pressure and temperature effects to rapidly dissolve the sediment. The most common methods use polytetrafluorethylene (PTFE or PFA) lined and sealed digestion vessels (Nakashima *et al.* 1988; Loring and Rantala, 1990). Since these closed systems retain the HF, boric acid is added after the HF digestion to complex remaining HF and make the resulting solution less hazardous, as well as preventing aluminium fluoride precipitation. The solution should be made up to volume with ultra pure water and left to stand for at least 24 hours prior to analysis to precipitate excess boric acid. Others use adjusted amounts of boric acid and heat the digest to accelerate the process (Maham *et al.* 1987). Typical methods are described, for example, in Cook *et al.* (1997), Jones and Laslett (1994), Wu *et al.* (1996), Quelle *et al.* (2011).

If HF is to be removed by evaporation, care should be taken to ensure that mercury is not lost from sample solutions (Delft and Vos, 1988). It can be difficult to avoid mercury contamination with total digestion, but usually mercury is not bound strongly, so mercury can alternatively be analysed using strong acid digestion or by direct analysis (Taylor *et al.*, 2012).

4.2 Strong acid digestion

Partial digestions follow broadly similar procedures to HF digestions, as described above, for example using HNO_3 or *aqua regia* and deionised water to ca. 0.5 g sample. Microwave digestion is the preferred technique, but alternative methods applying high pressure and temperature can be used. The method used needs to be checked. Adequate performance is achieved when the digestion dissolves all the Al and Li from the clay fraction. It can easily be tested whether a method meets this requirement through parallel analyses of very fine grained samples by the partial method in use and a total method e.g. HF. If results for Al and Li do not differ significantly, the partial method used is sufficiently strong. To optimise the tests and to further normalize results, sieving to 20 or 63 μm grain size can be used, also reducing problems with detection limits in sandy sediments. A more general discussion on normalization can be found in the Technical Annex 5: Normalisation of Contaminant Concentrations in Sediments.

If the partial method results in lower contents than the total method, the conditions for the partial digestion such as time, temperature, acid concentration etc. need to be adjusted. Usually boiling with *aqua regia* is insufficient for a complete dissolution of Al. Historically, *aqua regia* has been used for strong acid digestions, but hydrochloric acid produces interferences for multi-element analysis by ICP and Cd in graphite furnace, so concentrated nitric acid alone may be used as a substitute (Christensen *et al.*, 1982; Krumgalz and Fainshtein, 1989; Koopmann and Prange, 1991). However, collision or reaction cell technology in ICP-MS can be used to reduce the interfering effect of chloride and other multi-element interferences, down to levels of <1% mass overlap for double charged or multi-element species, thus minimising correction formulas for standard mass-corrections.

5. Analysis and detection

Analysis of metals in solution resulting from digestion may be performed by a variety of means, but usually involves spectrometric or spectroscopic detection. Flame or graphite furnace atomic absorption spectroscopy used to be the primary method for analysis of metals (Welz, 1985). Alternatively, non-destructive methods, i.e. XRF (e.g. Jenkins, 1999; Potts, 1992; Williams, 1987; Bertin, 1984; Parsons *et al.*, 2013) and INAA (Alfassi, 1998), which do not require a preceding digestion step, can be used. Multi-element techniques like inductively coupled plasma attached to either an emission spectrometer (ICP-AES) or mass spectrometer (ICP-MS) allow much more rapid analysis of a wide range of metals (Kimbrough and Lauenstein, 2006; Duzgoren-Aydin *et al.*, 2011; Castillo *et al.*, 2012).

Interferences in the analysis may arise through the presence of other components in the sample. Use of at least 3-point standard additions may highlight where these occur and can be used to correct for suppression or enhancement effects. Interferences occurring with multi-element analytical techniques can be complex and require skilled personnel to identify and minimise such effects (Cook *et al.*, 1997).

Mercury can be detected by fluorescence spectrometry or cold vapour atomic absorption spectrometry. Direct methods for analysing mercury use pyrolysis combined with a gold trap and fluorescence or atomic absorption detection are sensitive enough to measure sediments directly (Maggi *et al.*, 2009; Kelly *et al.*, 2012). ICP-MS is also sufficiently sensitive to measure Hg, but care should be taken about controlling carry over memory effects.

It should be ensured that the limits of detection of the analytical technique selected meets the requirements of the respective monitoring programme. Typical detection limits using different methods are given in Table 1.

Table 1. Typical limits of detection for the determination of trace metals with different techniques (in mg/kg d.w.) based on typical sample intakes (0.5–1 g)

	Al	Li	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
AAS / flame	5	0.2		0.5	5	2		5	5	10
AAS / graphite furnace, hydride technique, cold vapour	<1	<1	0.2	0.02	<1	<1	0.05	<1	<1	-
ICP – AES with hydride generation	10	10	10 1	0.5	1	1	-	2	5	1
ICP – MS	40	0.1	1	0.01	0.2	0.1	0.05	0.2	0.2	2
X-ray fluorescence analysis (XRF)	1000	-	-	-	10	10	-	10	10	20
Neutron activation analysis (INAA)	-	-	0.3	1	0.8	-	0.1	-	-	2
Fluorescence, AAS spectrometry (direct or cold vapour/hydride generation)	-	-	0.2	-	-	-	0.005	-	-	-
Direct Mercury Analyzer (AA)							0.005			

6. Metal speciation

Several methods are in use to examine metal speciation in sediments, mainly by use of sequential extraction (e.g. Gleyzes *et al.*, 2002; Scouller *et al.*, 2006; Sutherland, 2010; Duzgoren-Aydin *et al.*, 2011), but currently also by passive samplers (for metals primarily DGTs) in porewater (Peijnenburg *et al.*, 2014).

7. Limits of detection

The limit of detection for each metal is normally determined by analysing a blank solution (containing acid to the dilution it is present in the sample) at least ten times. The limit of detection is calculated from 3 times the standard deviation of the blank taken through the whole procedure. For typical limits of detection, see Table 1.

8. Calibration and standards

Calibrations are usually performed using multi-element stock solutions and at least a 4-point calibration covering the range of concentrations expected in the samples. Multi-element solutions are commercially available, and may be used provided that they are of a similar matrix to the analyte. A crosscheck solution from a separate batch, or from a different supplier or an internal reference standard, should be used to check the calibration. Differences should not exceed 10%.

For non-destructive methods, appropriate certified reference sediments are required for calibration purposes.

9. Quality assurance

Every determinand should have its own Quality Control and Quality Assessment (QC – QA) scheme that includes regular blanks and calibration checks, the use of internal reference materials and certified reference materials and quality control charts. A system suitability check should be included in each batch to confirm that the measuring instrument is operating correctly. In each batch of samples at least one standard addition (from the start of the digestion) should be included to demonstrate that matrix effects do not occur, and also a duplicate sample.

At least one laboratory reference material should be included in each batch of samples in order to check the long-term performance. A quality control chart should be constructed for selected trace metals. If the warning limits are exceeded, the method should be checked for possible errors. When alarm limits are exceeded, the results should not be reported.

Certified reference materials (CRMs) for sediments are commercially available for both total methods and partial digestion methods. The data provided by such materials allow an independent check of the analytical performance. Table 2 contains information on certified reference materials available for use in marine monitoring.

Table 2. Certified Reference Materials for metals in marine sediments.

Code	Organization	Matrix
BCR 277R	IRMM ¹	Estuarine sediment
BCR 320R	IRMM	Channel sediment
BCR CC580	IRMM	Estuarine sediment (only Hg and CH ₃ Hg)
BCR 667	IRMM	Estuarine sediment
HISS-1	NRC ²	Marine sediment
MESS-3	NRC	Marine sediment
PACS-2	NRC	Marine sediment (Harbour)
SRM 1646a	NIST ³	Estuarine sediment
SRM 1944	NIST	Marine sediment
SRM 2702	NIST	Marine sediment

¹IRMM: Institute for Reference Materials and Measurements (Europe)

²NRC: National Research Council (Canada)

³NIST: The National Institute of Standards and Technology (USA)

Participation in an international proficiency-testing scheme e.g. QUASIMEME is highly recommended to improve comparability between laboratories. Relevant quality assurance data should be reported e.g. to ICES, together with concentration data.

10 References

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Annex 6: OSPAR Technical Annex 4: Organotin compounds in sediment

This annex is intended as a supplement to the general guidelines. It is not a complete description or a substitute for detailed analytical instructions. The annex provides guidelines for the measurement of organotins in marine sediment in monitoring programmes. Organotins can originate from several sources. In addition to the previous use of antifouling agents on ship hulls, organotins can also be emitted to the environment from their use as fungicides or stabilisers for plastic materials (Fent, 2006; Fent and Muller, 1991; Hoch, 2001).

Target compounds include tributyltin (TBT), dibutyltin (DBT) and monobutyltin (MBT) and also triphenyltin (TPhT), diphenyltin (DPhT), and monophenyltin (MPhT). The method can be optimized to analyse other target organotins such as octyltins.

In order to assess the analytical results of organotin compounds in sediments, covariables must be measured as potential normalisers (e.g. grain-size distribution, organic carbon content, carbonate content). For samples 'diluted' with sand, the sample intake size can be increased. For very sandy samples, isolation of the fine fraction by sieving might be required.

1. Sampling and storage

Storage of samples is preferably done in glass, but containers of other materials such as polycarbonate or aluminium are also suitable. Nevertheless, possible adsorption of and contamination by organotin compounds need to be checked. Since photochemical degradation during storage has been reported for the aqueous phase (Quevauviller and Donard, 1991), the samples should be protected from light. Samples should be frozen after collection. For longer-term storage, the samples should be placed in a freezer (below -20°C) with or without freeze-drying. Under these conditions, samples can be stored for over a year (Gomez-Ariza *et al.*, 1994).

2. Transportation

Samples should be kept cool and ideally frozen below -20°C as soon as possible after collection. Sediment should be transported in closed containers at temperatures between 5 – 15°C , preferably $<10^{\circ}\text{C}$. Frozen samples should be transported in closed containers at temperatures below -20°C .

3. Blanks and contamination

The complete analytical procedure should be checked for blank values, i.e. all solvents, chemicals, and adsorptive materials should be checked for potential sources of contamination or interference. If a contamination has been localised, measures must be taken to avoid it (e.g., cleaning, different suppliers etc.).

Although butyltin compounds are not likely to occur in the laboratory environment or in solvents or most chemicals, commercial derivatisation reagents sometimes contain significant concentrations of various (butyl)tin species. This can be solved by purchasing from other suppliers or by preparing the reagent in the laboratory.

Glassware should be treated thoroughly with concentrated HCl or HNO_3 and rinsed with deionised water and acetone prior to use. Alternatively, the glassware can be

heated in an oven at 450°C or above after going through the standard glassware cleaning procedure.

4. Pre-treatment

Before taking a subsample for analysis, samples should be sufficiently homogenised. Especially samples from harbours can contain paint particulate matter irregularly distributed in the sample, thereby affecting the representativeness of the subsample. This can only be avoided when intensive mixing techniques (e.g. ballmill) are applied. Homogeneity can be checked by analysing several subsamples (e.g. five). Sediment samples from the marine environment are more homogeneous than those from harbour areas, as contamination in marine sediments usually derives from the water phase as mediated by tidal water movements. Less polluted samples are often more homogeneous than highly polluted samples. Because the size of the sample intake for analysis is inversely related to the pollution level, the intake will be small when the risk for heterogeneity is high. For this reason, multiple analyses might be appropriate for the higher concentration levels. The sample intake is usually around 1–5 g (dry weight), but some methods do not allow the use of more than 1 g (see also section 5.5).

Most extraction methods can deal with wet as well as dry samples. Analysis of wet samples saves laborious drying procedures, but dry samples are more easily homogenised and stored. In general, organotins can be analysed from the same sample collected to monitor other substances such as polychlorinated biphenyls (PCBs). Since mono-, di-, and tributyltin are ionic compounds and strongly sorbed to the sediment, it is unlikely that losses through evaporation during air-drying or freeze-drying will occur. Air-drying has been reported possible up to 50°C, but because other related compounds (i.e. phenyltins) decompose, freeze-drying is preferred (Gomez-Ariza *et al.*, 1994). Whichever drying procedure is used, the suitability with regard to cross-contamination and losses should always be tested (Quevauviller and Donard, 1991). If sieving is required, avoid contact with plastics. The use of stainless steel equipment is strongly recommended.

5. Analysis

5.1 Preparation of materials

Solvents, chemicals and adsorption materials must be free of organotin compounds or other interfering compounds (see also section 3). If they are not they should be purified using appropriate methods or replaced with clean materials. Solvents should be checked by concentrating the volume normally used in the procedure to 10% of the final volume and then analysing for the presence of organotin compounds and other interfering compounds by gas chromatography (GC). If necessary, the solvents can be purified by redistillation. Chemicals and adsorption materials should be purified by extraction and/or heating. Glass fibre materials (e.g. thimbles for Soxhlet extraction) should be pre-extracted. Alternatively, full glass thimbles with a G1 glass filter at the bottom can be used. Generally, paper filters should be avoided in filtration and substituted for by appropriate glass filters. As all super cleaned materials are prone to contamination (e.g. by the adsorption of organotin compounds and other compounds from laboratory air), materials ready for use should not be stored for long periods. All containers, glassware etc. which come into contact with the sample must be made of appropriate material and must have been thoroughly pre-cleaned.

5.2 Dry weight determination

Dry weight determinations should be carried out by air-drying homogenised sub-samples of the material to be analysed to constant weight at 105°C.

5.3 Calibration and preparation of calibrant solutions

5.3.1 Calibration

Multilevel calibration with at least five calibration points is preferred to adequately define the calibration curve. Standard preparation can be done in two ways depending on the methods of extraction/derivatisation used:

- i) by using alkyltins salts then proceed to the derivatisation step as for samples (for hydridisation or ethylation followed by purge-and-trap analysis, there is no other appropriate way than using alkyltin salts);
- ii) by using commercially readily available derivatised standards.

Standard solutions can be prepared in (m)ethanol or another solvent depending on the instrumental method used. Addition of an internal standard to all standard and samples solutions is recommended, e.g. tripropyltin chloride TPrTCl or ¹³C labelled or deuterated TBT if using GC analysis with mass selective detection. When using tripropyltin chloride, which is an underivatised standard, the recovery efficiency of the whole procedure can be determined.

A new calibration solution should always be cross-checked to the old standard solution.

Calibrant solutions should be stored in a refrigerator in gas tight containers to avoid evaporation of solvent during storage. It is important to determine the expiry date of standard dilutions in order to avoid a concentration shift due to deterioration of analytes or evaporation of solvents.

5.3.3 Isotope Dilution–Mass Spectrometry

Isotope Dilution–Mass Spectrometry technique (IDMS), can be used as an alternative quantification method (Monperrus *et al.*, 2003; Centineo *et al.*, 2004).

5.4 Extraction

Organotin compounds are strongly bound to particulate matter. The binding forces to the sediment have a dualistic character. Whereas tributyltin is mainly bound by hydrophobic forces, mineral binding dominates for monobutyltin because of its high electrical charge (e.g. the binding characteristic of trace metals). To achieve complete extraction, the butyltin compounds have to be released from the sediment, i.e. the binding must be diminished and the solubility in the extraction solvent must be maximised.

Different approaches can be applied to extract organotins from sediments:

- Acidic digestion followed by *in situ* derivatisation with simultaneous extraction to an organic phase.
- Leaching under acidic conditions with simultaneous extraction of the compounds to an organic phase, as applied with different acids, solvents and complexing agents.

To maintain a logical order, '*in situ* derivatisation' will be discussed as a derivatisation technique (see below) and not as an extraction technique. Furthermore, the use of recovery internal standards (RIS) to check the procedural steps is discussed separately below.

5.4.1 Acidic digestion followed by *in situ* derivatisation

Digestion techniques by adding hydrochloric acid or acetic acid can be used to extract organotins, while stirring or shaking the sample. Another possibility is the use of ultrasonic treatment.

5.4.2 Leaching and subsequent extraction to an organic phase

When extracting organotin compounds with an organic phase immiscible with water (e.g. DCM, diethylether, hydrocarbons etc.), much higher acid concentrations (6 M HCl) can be applied without obstructing the derivatisation. High acid concentrations will leach most of the monobutyltin from the sediment, but the high electrical charge of the monobutyltin³⁺ ion will not allow complete extraction to an organic phase. Under these strongly acidic conditions, the addition of complexing agents, e.g. tropolone (2-hydroxy-2,4,6-cycloheptatrienone) or diethyldithiocarbamate (Zhang *et al.*, 1991; Quevauviller, 1996) is not expected to have much effect. Just like the sediment, the agent will be protonated and consequently lose (much of) its complexation ability. When applied, the effectiveness of complexing agents should be critically evaluated. Furthermore, large amounts of agents in the extract may affect the chromatography.

Quantitative extraction of all butyltin compounds to pentane is possible only under strongly acidic conditions when HBr (6 M) is used (Gomez-Ariza *et al.*, 1995). The presence of bromide ions is essential to promote the extraction to the organic phase (pentane) through the formation of neutral ion-pairs. For tributyltin, it was shown that the distribution coefficient between octanol and water increased from 10² to 10⁶ after the addition of 1 M bromide (Weidenhaupt, 1995).

Gomez-Ariza *et al.* (1995) used a 'sediment:6 M HBr: pentane' ratio of 1:5:10 (g/v/v) for extraction. The leaching time was set to one hour, followed by an extraction of one hour. For completeness a second extraction with pentane is recommended. The pentane extract obtained can safely be concentrated, as the ionic butyltin compounds will not evaporate easily. This low risk for evaporation also allows transfer to other solvents if required for derivatisation or analysis. The residue can be subjected to chromatographic methods such as high performance liquid chromatography (HPLC) that directly analyses the butyltin compounds in their ionic form. For GC methods, the butyltin compounds are derivatised to their hydride or tetra-alkyl form.

5.5 Derivatisation

Derivatisation can either be performed after extraction or simultaneously with extraction.

Sodium Tetraethylborate (NaBEt₄): Derivatisation with this reagent has been developed to minimise the analysis time. The NaBEt₄ procedure allows a simultaneous extraction-derivatisation in a buffered medium (optimum pH 4-5). NaBEt₄ derivatisation produces more thermally stable derivatives. However, NaBEt₄ is extremely air sensitive, since it is considered as pyrophoric, care must be taken to keep its chemical integrity. Although solutions in water have been shown to be stable for about 1 month at 4°C, it is recommended to prepare them freshly for use.

Solutions of the reagent in an organic solvent (e.g. tetrahydrofuran, methanol or ethanol) seem to be more stable (Smedes *et al.*, 2000). After the addition of sodium tetraethylborate (e.g. 1 to 4 ml of 2 to 5 % solution in water or organic solvents), the mixture is shaken vigorously (Wilken *et al.*, 1994).

Although ethylation in the aqueous phase is very fast, the derivatisation is limited by the desorption kinetics. Multiple additions have been applied, but a continuous addition of the reagent using a peristaltic pump supported by effective mixing conditions is more appropriate. In this way, the reagent is always present and every butyltin molecule desorbed from the sediment is immediately derivatised and extracted, which also makes the desorption process continuous. However, this very intensive derivatisation may lead to the formation of boroxin, a six-angle ringed ethylborane. This compound is very reactive to the (bonded) phases used in gas chromatographic columns, affecting the column efficiency and mass spectrometric (MS) response. The boroxin is not removed by the normal phase column clean-up procedure usually applied, but can be degraded by the addition of an alkaline aqueous solution with a pH above 12. Ethylated organotin compounds will not be affected.

Since organic matter also reacts with the sodium tetraethylborate, the amount of sample that can be used is limited. As a rule of thumb, the sample intake should represent about 20–50 mg organic carbon which is, in practice, 1 g fine material (dry weight).

If simultaneous extraction and *in situ* derivatisation is used, 5 to 10 ml of organic solvent (hexane or pentane) has to be added before derivatisation. The extraction of the derivative itself is quantitative but to isolate the whole organic phase, a second extraction is necessary. Usually centrifugation is required to separate the phases.

Grignard reagent, sodium diethyldithiocarbamate (NaDDTC) and sodium borohydride (NaBH_4) are alternative derivatisation agents which can be used on organic phase extracts from sediment leachates. These reagents are not widely used anymore. Methods are described in Waldock *et al.* (1989) and Morabito *et al.* (2000).

5.6 Clean-up

Whether a clean-up step must be applied depends on the sample type, separation (GC or LC), and detection method used. Furthermore, the nature of the extract determines whether a clean-up step is possible. In the literature, no clean-up procedures are reported for aqueous/methanol leachates. Clean-up is not necessary when the butyltin compounds are determined by purge and trap analysis, which acts as a superb clean-up. However, extraction methods using an organic solvent will co-extract many kinds of other compounds from the sample, such as sulphur and sulphur-containing compounds, oil, and many other natural and anthropogenic compounds.

In addition to co-extracted substances, the extract will contain by-products of the derivatisation. Using sodium tetraethylborate for derivatisation, compounds such as boroxin, diethylsulphide, and diethyltrisulphide can be formed in rather large quantities (section 5.5). If the basic wash has not yet been conducted, it should be added here as a clean-up step. The ethylsulphides usually do not disturb the instrumental analysis. Also, co-extracted substances usually do not visually disturb the chromatogram because most detection methods are very selective. Nevertheless, a large amount of matrix in the sample can affect the chromatography when the loading capacity of the column is exceeded, and can influence the detector response (e.g. MS). A decrease in the amount of matrix is always favourable for instrumental analysis and therefore a clean-up is recommended.

Generally, a simple SiO₂, Al₂O₃ or Florisil column clean-up is sufficient for sample clean-up. Alkylated tin compounds are as non-polar as PCBs and elute rapidly with hexane. Nevertheless, highly activated materials are not recommended, as the organotin compounds may degrade during elution. Using 2 g of SiO₂ deactivated with 1–5 % water or Al₂O₃ with 5–10 % water in a glass column, organotin compounds usually elute in 5–10 ml hexane or pentane. Elution patterns should always be checked for each batch of column material.

5.7 Pre-concentration

Evaporation of solvents using a rotary evaporator should be performed under controlled temperature and pressure conditions, and the sample volume should be kept above 2 ml. Evaporation to total dryness should be avoided. To reduce the sample volume even more, e.g. to a final volume of 100 µl, solvents like pentane or hexane can be removed by concentration with a gentle stream of nitrogen. Only nitrogen of a controlled high quality should be used. Iso-octane is recommended as a keeper for the final solution to be injected into the GC.

5.8 Instrumental determination

Most of the analytical techniques developed for the speciation of organotin compounds are based on GC. GC remains the preferred separation technique owing to its high resolution and the availability of sensitive detectors such as (pulsed) flame photometry ((P)FPD), mass spectrometry (MS) or inductively coupled plasma- mass spectrometry (ICP-MS).

High performance liquid chromatography is an alternative approach. It mainly uses fluorescence, ultraviolet, and more recently inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), and mass spectrometry detectors such as atmospheric pressure chemical ionisation mass spectrometry (APCI-MS-MS) and electrospray ionisation mass spectrometry (ESI-MS).

ICP-MS and (P)FPD detectors, equipped with a 610 nm band-pass filter selective for tin compounds have been applied widely because of their inherent selectivity and sensitivity. (P)FPD has been shown to have greater selectivity and lower detection limits (by a factor of 25 to 50 times) for organotin compounds than those obtained with conventional FPD (Bravo *et al.*, 2004).

5.8.1 Gas chromatography

Possible injection modes are splitless, large volume and on-column injection. Automatic sample injection should be used wherever possible to improve the reproducibility of injection and the precision of the overall method. If splitless or large volume injection is used, the liner should be of sufficient capacity to contain the injected solvent volume after evaporation. Helium must be used for GC-MS, GC-FPD and GC-ICP-MS. The preferred column length is 25–30 m, with an internal diameter of 0.15 mm to 0.3 mm. Film thicknesses of 0.3 µm to 1 µm are generally used. The most commonly used stationary phase for organotin analysis is 5% phenyl methyl siloxane. Mass spectrometric analyses are usually conducted in electron-impact mode at 70eV.

5.8.2 High Performance Liquid Chromatography

All stainless steel parts of the HPLC system that come into contact with the sample should be replaced by polyether ketone (PEEK) components. Reverse phase columns (e.g. octadecylsilane C18) are commonly used (Wahlen and Catterick, 2003) and the mobile phase can consist, for example, of a mixture of acetonitrile, water and acetic acid with 0.05% triethylamine, pH 3.1–3.4 (65:25:10, variable depending on columns used).

6. Quality assurance

References of relevance to QA procedures include HELCOM (1988), HELCOM COMBINE manual, QUASIMEME (1992), Oehlenschläger (1994), ICES (1996) and Morabito *et al.* (1999).

6.1 System performance

The performance of the instrumentation should be monitored by regularly checking the resolution of two closely eluting organotin compounds. A decrease in resolution points to deteriorating instrumental conditions. A dirty MS-source can be recognised by the presence of an elevated background signal together with a reduced signal-to-noise ratio. Chromatograms should be inspected visually by a trained operator.

6.2 Recovery

The recovery should be checked and reported. It does not guarantee that extraction is complete for the more aged compounds already present in the sample, but nevertheless complete recovery is a minimum requirement for the assumption that extraction is complete. One method is to add an internal (recovery) standard to each sample immediately before extraction (e.g. tripropyltin) and a second (quantification) standard immediately prior to injection (e.g. tetrapropyltin).

Correction for recovery is advised against as it is most likely not representative of the actual recovery of aged compounds and is only a measure of how well the procedure has been performed. However, when it is local practice to correct for recoveries, three recovery standards (a mono-, di-, and trialkyltin) are required because of the different properties of the three butyltin compounds. The uncorrected values should be reported in brackets to show the elevation due to the recovery correction. Results of analyses that show recoveries lower than 50 % should be rejected or the samples should be re-analysed.

When using Isotope Dilution-Mass Spectrometry technique, the loss of target analytes is compensated. However, the recovery should still be calculated and should be between 50% and 150%.

6.3 Blanks

A procedural blank should be measured for each sample series and should be prepared simultaneously using the same chemicals and solvents as for the samples. Its purpose is to indicate sample contamination by interfering compounds, which will lead to errors in quantification. Even if an internal standard has been added to the blank at the beginning of the procedure, a quantification of peaks in the blank and subtraction from the values obtained for the determinands must not be performed, as the added internal standard cannot be absorbed by a matrix.

6.5 Accuracy and precision

A Laboratory Reference Material (LRM) or Certified Reference Material (CRM) should be included, at least one sample for each series of identically prepared samples. The LRM/CRM must be homogeneous, well characterised for the determinands in question and stability tests must have shown that it produces consistent results over time. The LRM/CRM should be preferably of the same type of matrix as the samples, and the determinand concentrations should occur in a comparable range to those of the samples. If the range of determinand concentrations in the samples is large (> factor of 5) two reference materials should be included in each batch of analyses to cover the lower and upper concentrations.

The data produced for the LRM/CRM in successive sample batches should be used to prepare control charts. It is also useful to analyse the LRM/CRM in duplicate from time to time to check within-batch analytical variability. The analysis of an LRM is primarily intended as a check that the analytical method is under control and yields acceptable precision, but a certified reference material (such as CRM 646 or PACS-2) of a similar matrix should be analysed periodically in order to check the method bias, ideally twice a year as a minimum. Additionally a duplicate of at least one sample should be run with every batch of samples. Each laboratory should participate in interlaboratory comparison studies and proficiency testing schemes on a regular basis, preferably at an international level.

6.6 Data collection and transfer

Data collection, handling and transfer must take place using quality controlled procedures.

7. Data recording and reporting parameters

The calculation of results and the reporting of data can represent major sources of error, as has been shown in intercomparison studies for organotin compounds. Control procedures should be established in order to ensure that data are correct and to avoid transcription errors. Data stored in databases should be checked and validated, and checks are also necessary when data are transferred between databases.

Data reporting should be in accordance with the requirements of the monitoring programme and with the latest ICES reporting formats. Results should be reported according to the precision required for the programme. In practice, the number of significant figures is defined by the performance of the procedure.

7.2 Analytical and quality assurance parameters

LRM and CRM results for a set of organotin compounds, reported on a dry weight basis; descriptions of the extraction, cleaning and instrumental determination methods; the detection limit for each organotin compound. Specific performance criteria, including detection limits and precision, are usually set by the programme. A typical detection limit for single contaminants is 1 µg/kg as Sn on a dry weight, although this might be difficult to achieve for phenyltins compounds.

QA information according to the requirements specified in the programme.

7.3 Parameters

Organic contaminants of interest to monitoring programmes for which these guidelines apply: butyltin compounds: tributyltin (TBT) and dibutyltin (DBT).

This technical annex also provides guidance on the determination of monobutyltin (MBT), phenyltin and octyltin compounds.

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Annex 7: Action list

AGENDA		
ITEM		
1	Bring information on existing methods dealing with PS in sediment for organic hydrophobic contaminants and metals	All members
1	Bring information on publications concerning toxicity of contaminants based on freely dissolved and on publication concerning sediment toxicity particularly with data related to sediment physiochemical characteristics	All
1	Report on ongoing and new projects involving passive sampling	All
2-4	Bring information on the new ToRs of the group: modelling, deep sea monitoring and renewable energy	All
5	Contact WGEXT for information on deep sea mining	Craig
5	Develop links up to relevant expert groups on marine litter	Céline

Annex 8: Technical minutes by RGMON

Technical peer review of material from ICES Expert Groups for OSPAR request concerning:

- A. 'Recommended method to determine the geographic representativeness of existing sediment monitoring stations' and
- B. 'Review and update of the Technical Annexes to JAMP Guidelines for Monitoring of Contaminants in Biota and in Sediments'.

Reviewers: Jos Brils (The Netherlands, chair), Paul Keizer (Canada), Carlos Vale (Portugal) and Jarle Klungsøyr (Norway).

Chair WGMS: Craig Robinson and Lucia Vinas

Chair MCWG: Katrin Vorkamp

Secretariat RG: Claus Hagebro

Review process

The Review Group (RG) conducted its work by correspondence, from 7 to 23 April 2014. The RG members reviewed the Expert Group (EG) material mentioned above independently, and then exchanged their summaries that were compiled by the RG chair to form the RG technical report, agreed by all. The RG report will be annexed to the EG material and considered by the ICES Advice Drafting Group ADGMON, meeting 28–30 April 2014.

The RG focused in its review on:

- The completeness of the EG material (and not on style or general editing);
- Whether the EG missed important points relevant to the request;
- Agreement or disagreement to any conclusions made.

Where the RG found that an aspect of the issue was overlooked entirely, the RG drafted text to address the point in question, including references.

General comments

The RG acknowledges the EG effort executing the tasks related to the above OSPAR requests.

However, it appeared to the RG that one part of the material that we reviewed, seems in significantly 'higher state of maturity' (i.e. the technical annexes 6 and 7 to JAMP guidelines for monitoring contaminants in sediments) than the second part of the material (i.e. the technical annex 2 to JAMP Guidelines for monitoring contaminants in biota as well as the recommended method to determine the geographic representativeness of existing sediment monitoring stations).

Hence, especially that second part of the material could benefit from further elaboration.

A. Method on geographic representativeness of existing sediment monitoring stations

The material provided by the EG starts by stating "*although several members of WGMS were present at MIME, they could not recall discussion of this subject and were unable to*

assist in interpreting the meaning of the question. As a result, WGMS 2014 had several different interpretations of the question that it decided to attempt to answer." Maybe a silly question, but why not have gone back to OSPAR for obtaining more clarity on the request – i.e. better framed the question(s) – before having started and executed the work?

Might this thus also be the reason why there is unfortunately very little advice for this request provided in the material?

The EG tackled several aspects of the request but along with other ICES EGs they are still uncertain as to how to deal with the issue of scale for the indicators of GES. The usefulness of statistical approaches, such as kriging, has been thoroughly explored and they provide some useful information. However one area that appears not to have been addressed is the potential usefulness of physical oceanographic circulation models that include simulations of the movement of the benthic boundary layer.

The only available information used by the EG to try to answer the questions raised by OSPAR was from southern North Sea. This is a highly dynamic area with shallow water depths (<50 m). It is well known from literature that strong and variable hydrographical conditions in this area lead to re-suspension and big sediment movements especially during stormy weather conditions. Both for spatial studies and for time trend studies it is generally recommended to sample sediments in areas where you have stable depositional conditions. You do not easily find these conditions in the southern North Sea. The RG feels that the EG should have commented on this in their report, and maybe also recommended to use data from other areas of the North Sea (e.g. the Norwegian Trench) when trying to answer the questions raised by OSPAR.

The specific request was *"Except for some work on sediment (Warren 1994, 1995), little is known of what geographical area each station represents. Given the current state of ocean models combined with measured changes at each station, OSPAR is requesting ICES (WGMS) whether a method can be recommended to determine the geographic representativeness of existing sediment monitoring stations."* The RG would take this to mean how much confidence do we have in contaminant distribution maps for sediments; i.e. what is the likelihood of missing a hot-spot or falsely identifying a hot spot, type 1 and type 2 errors? The RG notes in particular the phrase "(g)iven the current state of ocean models" which indicates to the RG that OSPAR is interested in knowing if and how these models might compliment the statistical approaches (e.g. kriging) to estimating concentrations between sampling locations. The RG would therefore support Q1 *"Suitability of sediment transport models to inform on the required spatial distribution of monitoring stations?"* as being the question of primary interest to OSPAR. Maybe it would be useful to recommend the application of normalisation to Al, Li or fine fraction, when extrapolation of metal concentrations between sampling locations are needed. That approach is valid to areas with a weak diagenetic signal in the surface sediments.

The sections on the "bubble plots" and concentration variability related to the size of a geographic area / strata are of limited usefulness. Both approaches are qualitative at best. The rationale for exploring concentration variability as a function of study area size is not apparent.

B. Technical Annexes for Monitoring of Contaminants in Biota and in Sediments

It would be useful for requests like this to update an existing document to either provide the original document or indicate the parts of the document that have been re-

vised. There are several references to recent publications in both documents indicating that parts of the documents have been updated.

Consideration should be given to also revising or creating the relevant TIMES documents to keep these documents current with the OSPAR guidelines.

Please note that this is a comment rather than a criticism of the text. In the introduction of each of the annexes it is noted that these annexes do not contain all of the detailed information needed to conduct specific analyses and directs the reader to more some detailed documents. It would be useful if there was some organization of the potential sources for detailed information on specific analytes or techniques, e.g. a table. Also in keeping with the suggestion that these updates be captured in the TIMES series, there are references to other technical annexes in this annex that for “non-OSPAR” laboratories can be difficult to access. The TIMES series is readily accessible on-line without charge or restriction and provides an editorial service to the authors to ensure the quality of the final document.

B1 - Annex 2: Metals in biota

Sections 1.1 – 2.2.2 seem to be in a significant less (too low?) state of maturity compared to the rest of the sections and could benefit from further elaboration.

Most critical issue is the (presumed?) relation between length and age. E.g. studying the appendix provided, it seems very difficult – not to say impossible – to ensure that a certain length matches to a certain age. Maybe there are better relations to be found in literature, but there are no references provided to such evidence in the provided material. Hence, statements like “*A sampling size range of xx – xx cm ensures individuals of the x-year age class*” (in **section 1.1.2** for flounder, hake and Pacific oyster) and “*selection of relevant length range in order to find individuals of the recommended age*” (**section 2.1**) seem to lack scientific underpinning.

B2 - Annex 6: Metals in sediments – analytical methods

The provided material appears to be complete and well laid out.

B3 - Annex 7: Organotin compounds in sediments

The provided material appears to be complete and well laid out.

The nature of the specific request from OSPAR should be included in the introduction, i.e. “*consideration should also be given to refocusing the butyltins method on dibutyltin as the primary determinant rather than tributyltin, as this compound is still widely used in e.g. plastics and clothing.*”

In annex 6 it often mentions that trained/skilled personnel are needed to perform the analysis. It seems that this is even more a prerequisite for performing the analysis as described in annex 7. But it seems to be less pronounced in annex 7.

Technical comments

A. Method on geographic representativeness of existing sediment monitoring stations

Q1

- It would be useful to have a physical oceanography group comment on this discussion. Considerable work has been done on the movement of particulate material in the water column and in the benthic boundary layer in relation to contaminant discharges from marine gas and oil exploration and production platforms. This type of approach would seem to be relevant here.
- The provided material states *“Existing understanding (of) hydrodynamic models can predict the dispersion of suspended particles from riverine input (e.g. Ferrer et al., 2009), but require input on the contaminant concentrations of these before they can be used to model the input of contaminants to a given sampling area.”* There is no further discussion or advice offered. Is it not possible that these models could be used to predict the distribution in the coastal zone of contaminants from riverine sources?
- *“... to trace the source of contaminated sediments ...”* or is it/should it no be *“to trace the source of the contaminations in the sediment”*?
- *“... but require input on the contaminant concentrations of these ...”* Of these: Of what? Anyhow a strange formulation *‘require input of the contaminant concentrations’* Please be more precise.

Q2

- This does not appear to be new advice but rather a reiteration of the advice provided in 2013
- Please each occasion you provide acronyms please also give full terms, so please do this for GES, ERL, EAC, MSFD
- *“... to obtain sufficient statistical power to assess concentrations against the assessment criteria ...”* You mean: *“... to obtain sufficient statistical power to determine whether there is a significant exceeding of the assessment criteria ...”*?
- *“... time trend monitoring ...”* Is this the ‘official’ JAMP jargon? If not, please for consistency use that jargon

Q3

- It is not apparent why there should be a relationship between the size of sampling area and the variability in the concentration. This would seem to be of little use to OSPAR
- Question not formulated precisely:
 1. be more specific on *“... concentration variability ...”*: i.e. variability of the

concentrations of contaminants in sediment?

2. "... relate to the size of a geographic area / strata ...": i.e. relate to the size and/or biophysical features of the sampling area and the number of sampled spots in that area?

- **Table 4.1:** Figure X should be Figure 4.1
- Page 3: "... Knowledge on the variability of concentration data for many more boxes ..." Please be more precise on "variability of concentration data"
- **Figure 4.2:** "Effect of spatial area ..." should it not be "Effect of the size of the sample area ..."?

Q4

- While this discussion is somewhat useful the RG feels that it suffers greatly from the omission of any discussion of the oceanographic processes dominant in the chosen areas and the potential sources of elevated contaminants in these areas. If elevated levels are observed then knowledge of the source of those elevated levels will contribute to the understanding of how the levels will vary in that area.
- Especially here the RG misses text that catches in a few words the key conclusions from the presented figures addressing Q4
- The text on the "bubble plots" is too qualitative to have any application to the request. The discussion on statistical estimation draws largely on the earlier work of Warren. There appears to be some benefit to certain types of statistical estimation but it should be done in the context of the knowledge that we have about the source of the contaminants and the physical and biological processes that influence their distribution. From a practical perspective an important question for the sampling design becomes how can I reduce the likelihood of a type 1 or type 2 error?
- Page 3: "... sediment contaminant and co-factor concentration data ..." Please mention (as example) some of these co-factors.
- Page 3: "... this may be due to a scaling effect." Please add 'to' and explain why it is due to that effect
- Page 3: "It is apparent that, as expected ..." Please explain why this was expected
- **Figures 4.4 – 4.6:** In header of these figures it indicates CORG, but below the figures it mentions total organic carbon. Is CORG same as TOC? If yes, for

consistency please use (preferred) TOC

- Why Pb contamination seems more evenly distributed over the North Sea than all other parameters, that show a tendency towards higher concentrations in Scheldt estuary and along the Dutch – Denmark coastline? Any explanation? Atmospheric deposition of Pb?

The summary (page 9)

- The answers to the questions could use some further elaboration, especially the answer to Q2 and Q4

B. Technical Annexes for Monitoring of Contaminants in Biota and in Sediments

B1 - Annex 2: Metals in biota

- **Section 1.1.1:** “... can only be selected in the light of information on fish stock composition and history ...”: How about shellfish?
- **Section 1.1.1:** “... Care should be taken that the sample is representative of the population ...”: Any suggestions on how to do that in practice?
- **Section 1.1.2:** “... To standardise results ...”: What does that mean? Please be more precise
- **Section 1.1.2:** “a. its migration is less pronounced, thus it is more likely to represent the area in which it is caught ...”: Please be more precise/explain this better
- **Section 1.1.2:** “*Mytilus edulis* occurs in shallow waters along almost all coasts of the Contracting Parties. It is therefore suitable for monitoring in nearshore waters”: Are all nearshore waters shallow?
- **Section 1.1.2:** “... *M. galloprovincialis* because the latter, which may occur along Spanish and Portuguese coasts, cannot easily be discerned from *M. edulis*”: what is/could be the implication of the fact that they cannot easily be discerned? In other words: do both species behave in same way if it concerns the uptake and accumulation of contaminants?
- **Section 1.1.2:** “For monitoring in polluted areas, mussels may be transplanted ...”: To make this more specific, insert ‘caged’ before mussels. Thus it relates to **section 4.3.1** of the generic part of the JAMP guidelines, where ‘caged mussels’ are mentioned.

- It would anyhow be good to make more references to the generic part of the JAMP guidelines
- **Section 1.1.2:** *"Flounder is not suitable for monitoring in open sea areas due to its migration pattern. ..."*: Please add a few words/explain that pattern.
- **Section 1.1.2:** *"Whiting It is a suitable substitute for cod."*: Why is that the case?
- **Section 1.1.2:** *"Hake The sampling size interval suggested is arbitrary and may need adjustment in the light of future experience."* Please elaborate, better explain why this is the case.
- **Section 2.1 as well as 2.2.1:** *"Gain in precision of the contaminant data ..."* Please elaborate, be clearer in what you mean here.
- **Section 2.1:** *"In selecting the sample, care should be taken to ensure that it is representative of the population and that it can be obtained annually"* Any suggestions on how to do that in practice?
- **Section 2.2.1:** *"... using biological variables. Although several biological parameters are appropriate ..."* Please either use variables or parameters.
- **Section 2.3.3:** *"...it is important to choose the egg from each clutch randomly."* Can you provide some guidance on how to do that?
- **Section 4.3.1:** *"..... sub-surface sea water."* Please be more precise: how deep is that?
- **Section 4.3.1:** *".....has not been subject to contamination from point sources."* How to ensure that?
- **Section 4.4:** *"The egg should then be opened"* Should that not be preceded by thawing? Thus sentence could then be *"After thawing the egg should be opened ..."*
- **Section 5.1:** Statements such as *"Glassware and Teflon equipment should be washed extensively with diluted nitric acid, distilled water and acidified metal-free deionised water"* need to be identified during the editing process. *"Diluted nitric acid"* and *"acidified metal-free deionized water"* need to be technically specified, e.g. 1N HNO₃.
- In general, the provided material requires extensive editing, e.g. *"calibrands"* is not a word.

- **Section 5.3.2 and 5.3.3:** especially here (more) references to more detailed analytical methods would be welcomed
- **Section 5.3.3:** full terms for GFAAS and TXRF are provided, please do same for all other acronyms in this section
- **Section 6.1:** *“the masses or concentrations of standards for the establishment of the calibration function must be prepared without bias.”* What does that mean: without bias? Please be more explicit
- **Section 7:** *“... the latest ICES reporting formats.”* Please provide the reference.
- **Appendix:** please add 1, so “Appendix 1”.

B2 - Annex 6: Metals in sediments – analytical methods

- **Section 1:** metals (first sentence) versus trace metals (rest of the annex 6): maybe give definition of trace metals and only/consistently use trace metals?
- **Section 1:** first sentence mentions ‘advice’. Maybe only use the word guidelines or guidance for consistency?
- **Section 1:** *“Analysis should be carried out by experienced staff”* Is it possible to be more explicit on what that means? What kind of level/training is required?
- **Section 1:** *“... procedure should be validated.”* What does ‘validated’ mean? Is it possible to be more explicit? E.g., is it recommended to use an ISO (or comparable) standard operation procedure?
- **Section 2:** *“For ordinary surveys ...”* What does this mean in terms of the generic part of the JAMP guidelines, i.e. to which types of monitoring of section 2 of those guidelines does it relate?
- **Section 2:** *“... for other purposes like retrospective surveys, ...”* Is a survey not always retrospective?: sediment that you sample now, has been deposited in the past, i.e. before it is sampled ...
- **Section 2:** *“Samples must be sieved to 2 mm after sampling ...”* Is total concentration to be expressed on fraction < 2 mm, or on weight of total original sample before sieving?
- **Section 2:** *“... other measured parameters may determine how to store the samples.”* Please provide a few examples of the “other measured parameters”.
- **Section 2:** is it possible to be more explicit (references to literature) on storage time of samples under specific conditions?

- **Section 2:** “*Air-drying is not appropriate due to*”. This is a deviation from the generic part of the guidelines where it mentions “*Alternatively, the sediments may be dried at any temperature below 105°C.*” Please make reference to that, i.e. that – if applicable – the generic guidelines are no longer appropriate regarding this aspect.
- **Section 5:** “*... skilled personnel ...*” Is it possible to be more explicit on what that means? What kind of level/training is required?
- **Section 9:** “*... demonstrate that matrix effects do not occur ...*”. Can you be more explicit in what “*matrix effects*” means in this context?
- **Section 9:** “*When alarm limits are exceeded ...*”. Can you be more explicit on “*alarm limits*”?
- **Section 9:** “*... such materials allow an independent check ...*” Can you be more explicit in what “*independent*” means in this context?

B3 - Annex 7: Organotin compounds in sediments

- **Section 1:** “*... possible adsorption of and contamination by organotin compounds need to be checked ...*” Can you give an indication/reference to a method on how to do so?
- **Section 2:** First sentence mentions “*Samples*”. Then second sentence continues with “*Sediment*”. Samples and sediment mean the same thing in this context? If yes, try to be more consistent in word use.
- **Section 5.8:** Please use complete terms for each abbreviation when mentioned first time: e.g. gas chromatography (GC). PFPD seems to be abbreviation of ‘pulsed flame photometry’. But where does the “D” then stand for?
- **Section 5.8.1:** “*... The preferred column length is 25–30 m ...*”. This should be ‘mm’ we suppose?
- **Section 5.8.2:** “*... mixture of acetonitrile, water and acetic acid with 0.05% triethylamine, pH 3.1–3.4 (65:25:10, variable depending on columns used) ...*” For readability please change to “*... mixture of acetonitrile, water and acetic acid (65%:25%:10%, variable depending on columns used) with 0.05% triethylamine, pH 3.1–3.4 ...*” And please note that we suggested to add ‘%’.
- **Section 6.1:** “*A dirty MS-source ...*” What is that?

- **Section 6.1:** *"Chromatograms should be inspected visually by a trained operator"*. Is it possible to be more explicit on what that means? What kind of level/training is required? And please also see the general comments related to this aspect.
- **Section 6.3:** *"... interfering compounds ..."* Can you please give a few examples of such compounds?
- **Section 1:** *"Even if an internal standard has been added to the blank at the beginning of the procedure, a quantification of peaks in the blank and subtraction from the values obtained for the determinands must not be performed, as the added internal standard cannot be absorbed by a matrix."* This sentence needs more explanation.