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2–7 March 2009

Galway, Ireland



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Executive summary

The Working Group on Marine Sediments in Relation to Pollution (WGMS) met from 2–7 March in Galway, Ireland. The meeting was chaired by Patrick Roose and Lucia Viñas and attended by 15 scientists from 11 countries.

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

The group reviewed the latest OSPAR MON assessment and the developments of sediment guidelines in relation to the Water Framework Directive. In both cases, comments were made that can be forwarded through the proper channels.

The background concentrations (BCs) for alkylated PAHs proposed at last year's meeting were evaluated in the light of additional information. No changes were made. Given the scarcity of the information in general, the BCs should be considered as preliminary. More information is needed to bring this task to an acceptable ending.

No values could be suggested at the meeting for the BCs of dioxins in sediment. The available information was listed during the meeting but data on dioxin concentrations in deep core sediments are sparse, and are required to set the values.

A number of requests for revision of Technical Annexes from OSPAR had been received during the 2008 meeting. Work on all of them continued, in collaboration with MCWG, and the final draft of the technical guideline on planar CBs in sediment should become available after MCWG. An initial draft of a Technical Annex on the measurement of dioxins in sediment was prepared during the meeting. The final draft will be presented at next year's meeting.

A subgroup lead by Ian Davies made considerable progress on reviewing the existing OSPAR Technical Annex on normalisation of concentrations of contaminants in sediment. A new Technical Annex was prepared at the meeting and it is recommended that this is forwarded to OSPAR for adoption.

1 Opening of the meeting

The 29th meeting of the Working Group on Marine Sediments in relation to Pollution was opened by Mr. John Evans, Director of Marine Environment and Food Safety Services, Marine Institute, Ireland. After a very informative presentation on the Marine Institute, he welcomed the WGMS and wished everybody a pleasant stay and fruitful meeting.

At the opening, the Chairs informed the group (Annex 1) about the recent developments in ICES concerning both the advisory process and the scientific programme. Some members of the group were interested in additional information, which was subsequently made available by the Chairs on the SharePoint site.

2 Adoption of the agenda

After briefly going through the agenda, given in Annex 2, it was accepted without modifications and arrangements were made to carry out the work.

3 Review and comment on the report of the data assessment from the 2008 meeting of OSPAR/MON in relation to sediments

3.1 Presentation on output of OSPAR MON 2008/2009 CEMP Assessment with modifications at HA-6

A summary of output of OSPAR MON 2008 was presented by Ian Davies. A number of maps were shown which demonstrated the use of a “traffic light” approach to illustrate the geographical distribution and temporal trends in the concentrations of contaminants. The presentation also outlined the basis for selection of transition points for assessing the data. It was highlighted that the presentation methods were developed specifically for the purpose of the JAMP HA-6 assessment on the development of the quality status of the marine environment and with the intention of providing an accessible synthesis of the CEMP assessment results for use in Chapter 5 of the Quality Status Report 2010. The output from the 2008 OSPAR/MON meeting was forwarded to the HA-6 meeting at the end of January 2009.

The results of the assessment are presented in an aggregated form rather than station by station maps, taking into account the aim of the OSPAR Hazardous Substances Strategy i.e. “to prevent pollution of the maritime area by continuously reducing discharges, emissions, and losses of hazardous substances with the ultimate aim of achieving concentrations in the marine environment near background values for naturally occurring substances and close to zero for man-made synthetic substances”. During the assessment, results were aggregated for lead, mercury, cadmium, CBs and PAHs as these are included in OSPAR’s list of priority substances and also due to the availability of many years of quality assured and consistent CEMP monitoring data. The 5 OSPAR regions were used for the initial division of the OSPAR area and each OSPAR region was then sub divided into “coastal” (<12nm) and “offshore” (>12nm) sub regions. Four levels of integration were then used.

Level 0 integration – aggregation to contaminant groups for PCBs and PAHs

Level 1 integration – aggregation of matrices

Level 2 integration – percentages from level 1 integration were averaged across sub regions

Level 3 integration – percentages from level 2 integration were averaged across contaminants at both a sub regional and regional level.

Tables were produced during each of the integration steps and the data was then used to generate bar plots which consist of a continuous bar and a series of histograms which are coloured to represent the status in the region/sub region (Red – unacceptable status, Green – status is acceptable, concentrations are above background and Blue – status is acceptable, near background concentrations). The length of the coloured parts of each continuous bar represents the percentage of the combinations of contaminants and matrices in each region/subregion that are classified as each colour.

The WG discussed this approach used and concluded that the original graphical representation produced at OSPAR MON was more informative than the assessments produced at HA-6 and that the quality of the data produced is lost when aggregated in the histograms.

3.2 Review of the Draft Report on the 2008/2009 CEMP assessment: Trends and Concentrations of selected hazardous substances in the marine environment.

This report relates to the review of the Draft Report on the 2008/2009 CEMP assessment: Trends and Concentrations of selected hazardous substances in the marine environment. Although the document is still in draft, a small subgroup of WGMS members not involved in the CEMP assessment reviewed the current version of the document, which was available at the time of the meeting (Version 1 draft 5). The comments/suggestions of this subgroup relate to the presentation of the data rather than the content. The group agreed that the data were well presented and that as in previous MON assessments, the use of symbols and colours to indicate the various types of trends and status allows the findings to be easily understood. The content of the report is largely consistent with that in previous years, with the exception of Section 12 - Aggregated assessment of quality status in relation to hazardous substances. Editorial comments are tabulated below.

SECTIONS & COMMENT

2. Matrices and Parameters covered in the assessment

a. metals – final line. Replace “arsenosucre” with “arsenosugars”

3. Methods

Paragraph 2 – first line. Replace “assessment criteria used are re-produced at Annex 1” with “assessment criteria used are presented in Annex 1”

5. Overview of data

Replace “recent cruses” with “recent cruises”

6. Description of basic outputs from the assessment

Page 8 – paragraph below table and Page 9 – final paragraph in section 6. Replace 2002 with 2003 and 2006 with 2007. Samples collected between 2003 and 2007 that did not form part of a time series were used to provide greater spatial coverage. Suggest using 2003 – 2007 in all cases to avoid confusion. Is text need twice?

Table in page 8 outlines colour coding used (Red, Green, Blue) and what each colour symbolizes. However the final paragraph in section 6 states that the data are coloured green, amber and red. Both sets of colour coding are then used in the maps in Section 7. For example, Figure 2 Page 11 amber instead of green? This should be explained better in the text or amber should be replaced with green?

7. Status and trends of heavy metals

The text explains that the first two maps indicate geographical distribution and the second two indicate temporal trends. In the case of cadmium, lead and mercury maps, it appears that Blue, green & red coding is used for sediments and blue, amber and red coding is used for biota. The text introducing section 7 states that blue, green, amber and red are used. Perhaps the colour coding could be better explained in the text or in table form.

The group recommends that there should be some general description of the status after each metal as is the case for PCBs and PAHs? Suggested text given at end of table.

8. Tributyl tin

Table on page 20 - Is it possible to just have the Nucella and Littorina to represent the biological effects data, that would account for class A to F on the biological effects side, and leave a better overview of the mussel, water and sediment correlation. Reference to 3.1 for the other families of snails if it is intended to make sure the public

Page 21 Figure 3– where did all the imposex data from the time trends go? Is this map only sediment and biota?

Page 21 text – replace “potemntial” with “potential”

10. PAHs

Page 26 final paragraph – last sentence. Replace “somje” with “some”

Page 27 paragraph – replace “ER-L” with “ERL”

11. Lindane

Page 30 – last line of text. Amend sentence to include reference to sediments. “There are insufficient time series of data to make any statements on temporal trends for sediments in the OSPAR area.”

12. Aggregation assessment of quality status in relation to hazardous substances.

Levels of Integration – general comment

Keep heading format consistent - use same format for headings for Level 2 and Level 3 integration as was used for level 0 and level 1 i.e. insert explanation of integration in the title. Currently the headings read as

- Level 0 integration – aggregation to contaminant groups for PCBs and PAHs
- Level 1 integration – aggregation of matrices
- Level 2 integration
- Level 3 integration

Page 33 Final paragraph – states that it defaulted to worst case for PAH and PCB, has this not been changed to 2nd worst case?

Page 34 – significant upward/downward trends – what statistics were used to check if significantly more upwards than downwards?

Page 39 – final paragraph. Replace “PAh” with “PAH”

Status and trends of heavy metals – suggested text

Cadmium concentrations in the arctic part of the North Sea and central North Sea are mainly at background in sediments (figure 1). Around the top of Scotland, most concentrations are at background or below the ERL, whereas around Ireland and along the the British Channel all the way up to Denmark, values are above ERL in most coastal sites, dropping to below ERL in the more open waters. Only some hotspots around England are above the ERL. For Region III, most Spanish data are above background but below ERL, except two known hot spots. The same picture applies for mussels, except the area around Island where some hot spots, probably due to volcanic activity, are found. Around Ireland, some areas with concentrations at background are found on the west coast, but mainly, concentrations above background but below EC levels are found. Concentrations around the British coastline are also generally below EC levels, and only a few hotspots are found along the British channel and in the bay of Biscay, where most concentrations are at background. Around Denmark most concentrations are above EC levels or between background and EC levels.

The time trends in sediment and biota are generally inconclusive, as both upwards and downward trends are found around the whole of the convention area. Around UK, most of the trends in sediment are upwards, whereas mussels are approximately half and half.

4 Review developments in the use of QUASIMEME information in the interpretation of field data on the ratios of contaminant concentrations

This work started at the WGMS 2007 meeting where a subgroup examined the spatial distribution of contaminant ratios (PAHs, PCBs) with respect to systematic deviations in the measurement results corresponding to the geographical ranges of national monitoring programs (ICES WGMS 2007 report). Indeed in some cases an apparent change in ratios was observed to coincide with boundaries between data from different countries in the same general area (e.g. Southern Bight of the North Sea). The investigation was based on Laboratory Performance Studies in the QUASIMEME Project since 2000. The aim was to explore whether there are systematic deviations between measured contaminant concentrations (ratios) within identical QUASIMEME samples and whether this correlates with differences observed between national monitoring programs. Measured contaminants ratios were normalised to the

mean contaminant ratio calculated for each QUASIMEME round, i.e. equivalent samples.

As recommended in the ICES WGMS 2007 report, these normalised values have been further used in an intersessionally work (Stefan Schmolke) for the assessment of systematic deviations in the performance of national laboratories with respect to the contaminants under investigation. The normalised ratios computed from the QUASIMEME samples were used to correct monitoring data. As illustrated on Figure 4.1 for the monitoring data along the southern coastline of the North Sea, the differences observed for the Phenanthrene/Anthracene (PA/ANT) ratio seemed to correlate with results from the QUASIMEME Laboratory Proficiency Schemes. The correction of the monitoring data by the normalised ratios led to a more homogeneous spatial distribution of the PA/ANT ratio along the Belgium Netherlands coast.

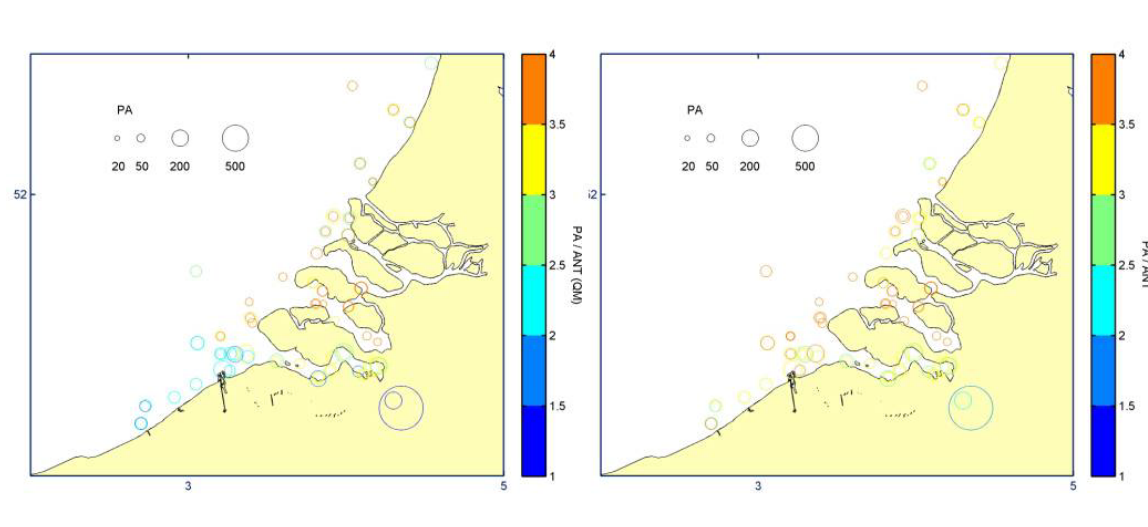


Figure 4.1. Phenanthrene/Anthracene (PA/ANT) ratio: Monitoring data along the Belgium Netherlands coast (left hand)/ Monitoring data corrected by the normalised ratios computed from the QUASIMEME samples (right hand).

After a brief discussion on this topic, WGMS:

- confirmed the WGMS 2007 evaluation of the scientific potential of the ratio method to assess differences in regional source patterns
- proved the potential of the QUASIMEME results to correct systematic biases in contaminants ratios of national monitoring data.
- proposed to postpone any further assessment of the ratio method to the period after QSR 2010.

5 Review and report on a survey of metals in North Sea sediments in relation to Background Concentrations carried out by Germany

Stefan S presented preliminary results from an impressive German initiative focussed on the presence and distribution of metals in the North Sea area.

The current German routine monitoring of metal burden in surface sediments (2 cm) covers 25 Stations spread over the German exclusive economic zone (EEZ). Samples are taken once a year since the late 1970s. Within the routine program all sediment

samples are size fractionated, and the metal concentration is measured in the fines (<20µm) fraction. Both, total digestion (HF), and strong partial digestion (HNO₃) are used for extraction of Al, As, Co, Fe, K, Mg, Ni and Ag, Cd, Cr, Cu, Hg, Li, Mn, Pb, V, Zn, Si respectively. The companion parameters total organic carbon (TOC), total nitrogen (N) and the percentage of the <20µm fraction were also measured. Based on the monitoring data, spatial and temporal trend analyses are performed to derive information about the quality status of the marine environment. To set the routine sediment monitoring into a North Sea wide context, Germany carried out an extended sediment sampling cruise in August 2006. Approximately 30 additional sampling sites across the entire North Sea (51.5°N – 58.0°N, 1.0°W–8.0°E) were covered. Due to the currently limited laboratory capacity the treatment of these additional samples is still under process. An overview of the results, so far available, was given, and implications for the further development of background concentrations and normalisation procedures were discussed.

The central North Sea is dominated by sandy sediments with a low content of fines (<5%). Certain elements like lead or chromium were found to be highly enriched in the fines in this region. In general, the elements Al and Li, which are commonly used as normalisers, display a less pronounced spatial pattern than some highly anthropogenic-influenced elements, like mercury. Nevertheless, a gradient, with a factor of about 2, between central North Sea samples and north-westerly coastal sites was observed. The TOC content in the fines fraction, commonly used as normaliser for organic contaminants, even displays a variation by a factor of about ten between the lowest and the highest concentrated samples. The spatial TOC pattern in the fines displays no correlation with that of Li and Al, but appears correlated with the total Nitrogen content.

The normalisation to the fines fraction was proven to be successful in the German Bight and North Sea data set. Even in sandy sediments a significant lineary decreasing mercury time trend was detected NW and SW of Helgoland. The normalisation to the fines fraction (by sieving to <20µm) led to a significant reduction of uncertainty in the prediction of time trends.

In the discussion afterward, the UK suggested to supplement the German dataset with additional metals in sediments data around the UK, measured in the <63 µm fraction. A more elaborated picture of the metal pattern in surface sediments of the entire North Sea will be developed, and could be used as a base for a regionalisation of normalisation procedures and assessment procedures. This will be taken up in WGMS 2010.

6 Review new developments at the EC level on the development of guidelines for monitoring of sediments in relation to the water framework directive

6.1 Activity on sediment monitoring in the EU

Ian Davies reported that the EU Directive 2008/105/EC on environmental quality standards in the field of water policy (the EQS Daughter Directive) required that Member States undertake monitoring of sediment and/or biota in relation to the Water Framework Directive.

Specifically,

- Member States may choose to develop and adopt EQSs for contaminants in sediment and biota, provided that they are at least as protective as the EQSs for water included in an Annex to the Directive.
- Member States are required to arrange for the long-term trend analysis of concentrations of those priority substances listed in Part A of Annex I to the Directive that tend to accumulate in sediment and/or biota. Member States shall take measures aimed at ensuring that such concentrations do not significantly increase in sediment and/or relevant biota.

In order to develop Guidelines on how Member States might best carry out such monitoring, a group was formed in 2008 under the CMA for the WFD. It initially met briefly in May 2008, and then has had a more substantive meeting in January 2009 in Ispra. Several members of WGMS were at the meeting, some representing their countries others representing OSPAR and/or ICES.

The Group is co-chaired by France and Italy, and the membership is dominated by marine scientists, in contrast to many other WFD groups. It was clear that the requirements under 2008/105/EC for temporal trend monitoring and for comparisons against assessment criteria were very similar in principle to the requirements of monitoring of contaminants in sediment and biota for OSPAR CEMP. Members of WGMS had provided copies of relevant ICES and OSPAR documents to the CMA group prior to the meeting, and many of the ideas and procedures currently recommended and used in OSPAR programmes were evident in the draft report and annexes discussed in Ispra.

WGMS agreed that the principle of trying to make the Guidelines resemble the OSPAR Guidelines as closely as possible, particularly for marine areas, should be supported. This would be increasingly important in the implementation of the Marine Strategy Framework Directive.

6.2 EQS for sediments

The last draft of the EU guideline for deriving EQS, Chemicals and the Water Framework Directive: Technical Guidance for Deriving Environmental Quality Standards, circulated for commentary to the member states February 2009 was examined by the group.

The sections relating to sediment were presented, and it was shown that there were some inconsistencies in the text.

The opening statement was, that EQS's are determined at a EU-wide level for priority substances and priority hazardous substances. Going into the text, it appears that sediment EQS's are only to be developed for benthic biota (with an opening later to also include secondary poisoning for substances where sediment is the main source for predator species). There is clear advice on prerequisites for developing sediment EQS (K_{oc} or $K_{ow} > 3$, evidence of accumulation in sediment or evidence of high toxicity in benthic organisms).

Considering the development of EQS, "when appropriate", the document goes on to discuss the necessary supporting information, like partition coefficients for octanol-water, suspended matter-water, sediment-water and organic carbon-water, water solubility, vapour pressure, photolytic and hydrolytic stability and molecular weight. Some of these are meant to check reliability of ecotoxicity experiments that form the base of setting the EQS, whereas others are related to recalculating between sediment

and water EQS's. It is also clearly stated that EQS for sediments are only for long-term standards.

The aim of an EQS for sediment is to protect sediment-dwelling species or other organisms from secondary poisoning, the main role is therefore to identify sites at risk of chemical deterioration, trigger assessment studies which may lead to programmes of measures, and identify long-term trends in environmental quality to check if the WFD's non-deterioration principle are upheld (for this an EQS does not seem necessary though).

The guideline warns that a lack of data and a less matured science behind the sediment EQS could lead to problems. Accordingly, policymakers should consider the most appropriate application for sediment EQS, e.g. is it appropriate to implement them as statutory instruments or long-term trends in contamination. Also, a stepwise approach to implementation where sediment EQS are considered triggers for further investigations are envisioned. The overall EQS does not include sediment EQS, so the trigger function can be viewed as the most important.

In the implementation of sediment EQS for organic substances, the guideline suggests a normalisation to 5% organic carbon content and no acid volatile sulphides. The emphasis is also on ecotoxicological data, allowing identifying concentrations below which harmful effects on sediment-dwelling species are not expected, like threshold effect level (TEL), effect-range low (ERL) and sediment quality advisory levels. Results based solely on equilibrium partitioning are, in this respect, not considered to be reliable. Assessment factors of 10 – 10000 should be applied, depending on the quality and extent of the ecotoxicological dataset. For lowest factor (10) there should be at least 3 long-term studies, including at least 2 marine species, with different living and feeding conditions, and, NOEC or EC10 data.

Additionally, if bioaccumulation or biomagnification occurs for a substance, direct effects might not be restrictive enough, and if sediments are the primary source of exposure, sediment EQS should be developed from biota-EQS. For metals, sequential extraction (SEM) and acid volatile substance (AVS) are put forward as a way to establish bioavailability of metals in sediments. The group discussed the principles of this at some length, and found the 1M cold HCl extraction was too weak and dependant on actual sediment content of e.g. CaCO_3 . It was suggested by Ingemar that 2.3M HCl more accurately described the stomach pH of marine animals, but the actual concentration chosen would not change the dependency of actual sediment content on the result. Also the AVS was not a standard parameter in most laboratories, and would require a re-evaluation of existing monitoring programmes. The inclusion of other biotic ligands would require modelling, and there either data or EQS value should either be normalised to 5%OC/no AVS, or local EQS should be set (in contrast to the opening statement about EU wide EQS). The possibility of establishing bioavailability fractions using passive samplers was considered a more viable way forward by the WGMS than the suggested SEM-AVS method, but with some adjustment of the methods and interpretation of results needed.

The inclusion of background levels for metals was very much along the lines of OSPARs way of defining background/reference concentrations (i.e. pristine areas or sediment cores), but alternative methods for setting background concentrations by geological modelling or modelling from water background concentrations using partitioning equilibrium models (which was not to be used for setting firm EQS values) was also suggested. EQS values below background levels were not considered scien-

tifically sound, and an added risk approach, albeit difficult to obtain was considered more appropriate.

During its discussion, WGMS found the current guideline somewhat lacking and that there was room for considerable improvement. The overall impression was that sediment-EQSs were made unattractive because of the many pitfalls in establishing them, and the fact that they would never be part of the overall EQS for a given site. The use for long-term (time trend) was considered reasonable, but would not necessarily advocate the use of sediment-EQS, and, in all probability, the guideline as it stands would result in a series of local/regional sediment EQS in contrast to the stated objective of EU-wide applicability. To this end, a more rigorous normalisation procedure than 5% OC and SEM-AVS should be produced. Alternatively, more focus on the use of passive samplers for measuring the bio-available fraction in pore water could be a way forward.

7 Investigate if the proposed background concentrations of alkylated PAHs in sediment need to be updated in the light of this assessment and new data supplied intersessionally

In 2008 WGMS investigated if the BCs for alkylated PAHs could be updated in the light of new data supplied data i) C1-, C2- and C3-naphthalenes; ii) C1-, C2- and C3-phenanthrenes, and iii) C1-, C2- and C3-dibenzothiophenes, and parent dibenzothiophene.

The data covered only a limited number of geographical areas from Scotland, Norway and France and some data from the Baltic were used to propose Background Concentrations. WGMS 2008 as well as 2007 recognized that these Background Concentrations had been obtained from very limited datasets and recommended that work be undertaken to extend the data set underlying these estimations, to an if available to include data from other areas, such as the Baltic Sea.

In the intersessional period, after the WGMS 2008 however only one new dataset became available. This was a core taken in the Skagerrak within the framework of the HARBASINS project that could be dated up to 1800. The dataset however did not include organic carbon data but did include other normalisers like Li and Al. On the basis of those normalisers in comparison with data from the Danish national monitoring in that area an organic carbon content of 3% could be derived. The HARBASINS core in the skagerrak contains in addition to a number of alkylated PAHs data on metals, PCBs, BDEs, parent PAHs, and some chlorinated pesticides. Al sediments from the core can be considered as very fine material based on the Al and Li concentrations of respectively 50 g/kg and 60 mg/kg.

The concentrations for alkylated PAHs appeared to vary very little with the depth. Concentrations in recent years were only up to 20% higher than in the deepest slices of around 1800. Table 7.1 shows that the concentrations are about one order of magnitude higher than the proposed background concentrations set in 2008. On the basis of this large difference the WGMS decided that it would not update the present proposed background values but add the data to the underlying data. The unexplained large difference between the new data and the proposed BC values indicate that more knowledge and data is required to give a sound basis to BC values for alkylated PAHs in the marine environment.

Table 7.1. Measured values for a few alkylated PAHs in sediments of a Skagerrak cores within the HARBASINS project and the 2008 proposed Background Concentrations, expressed as concentrations normalised to 2.5% organic carbon.

Parameter	Skagerrak core Concentrations normalised to 2.5% organic carbon (ug/kg dry weight)	2008 proposals for Background Concentrations normalised to 2.5% organic carbon (ug/kg dry weight)
NAPC1	20	2.7
NAPC2	45	6.7
PAC1	80	2.7

8 Continue collection of data and develop background concentrations for dioxins. (OSPAR Request 4, 2008)

Following the intention of OSPAR to include dioxins in their sediment monitoring programmes, it is necessary to establish Background concentrations for subsequent assessment of monitoring data. This work was initiated last year leading to a first collection of data on concentrations of dioxins in sediments from different areas:

A subgroup of WGMS continued to examine a number of scientific papers in relation to this topic. Difficulties were encountered in the relative paucity of data from deep sediment cores or potential background situations. Data were gathered in two different tables (Tables 8.1 and 8.2) corresponding to sediment and soil data respectively.

As highlighted last year, it is important to note that these values are not considered to be background concentrations; they are more a summary of dioxin concentrations reported for individual areas.

WGMS found:

- 1) That these new data covered a wide geographical areas (Europe (mainly the North part), Asia and Australia);
- 2) That these data correspond not only to marine sediments but also freshwater sediments: (A special table on data on soils was also presented for comparison);
- 3) That some of the contaminant data were not accompanied by appropriate data on cofactors.

WGMS concluded that the data collected so far were not yet sufficient to allow a reliable expression of background conditions and recommends that work be undertaken to collect other data and their appropriate cofactors.

Table 8.1. Preliminary table of concentrations of dioxins in sediment

AUTHOR	REFERENCE	LOCATION	SEDIMENT DEPTH CM	SEDIMENT AGE	PCD D PG/G D.W	PCDF PG/G D.W	PCDD /F PG/G D.W	TEQ- PCDD PGTEQ/ G D.W	TEQ- PCDF PGTEQ/ G D.W	TEQ- PCDD/F PGTEQ/G D.W	TOC %	COMMENTS
N-EPA, 2008	SFT, 2008	Norway	0–2							<10		National marine sediment criteria, mud
Isosaari	Chemosphere, 2002, 47, 575	Finland	0–11	1999-1790			84			1.18		Freshwater
Kjeller	Environ. Sci. Technol., 1995, 29, 346	Sweden	26–28	1882	37	55	92					Marine
Jonsson	Ambio, 1993, 22, 37	Baltic	30–35		215	60	275					Baltic sediments
Götz	Chemosphere, 2007, 67, 592	Germany	40–45	< 1946	343	519	862			20		Middle Elbe River
			135–150	< 1946	648	69	717			2		River Elbe – Hamburg
Ricking	Marine Pollution Bulletin, 2005, 50, 1699	NE- Germany	46	< 1900			329				6.5	Marine
			36	< 1900			19				36.5	Lake Bugsin
			233	< 1900			79				6.5	Lake Quenz
			95	1944			97				15.1	Lake White
Frignani	Environ. Int., 2005, 31, 1011	Venice	40	1840						0,02–47		Venice lagoon
Gauss	Environ. Sci. Technol., 2001, 35, 4597	Australia	136–140	1944	1000	7	1007				0.67	Marine
			324–326	1867	760	3	763				0.65	
			372–376	1843	850	7	857				0.67	
Mueller	National DioxinProgram, tech. Report 6, 2004	Australia	Surface				150			0.2		Median, all freshwater
			Surface				1500			2.3		Median, all estuarine
			Surface				33			0.12		Median, all marine
Green	Environ. Sci. Technol., 2001, 35, 2882	UK	core	1850	131	21	152					Rural freshwater lake
Okumura	Water Res., 2004, 38, 3511	Japan	28–30	1934	377	10	387	0.73	0.28			Marine
Pan	Chemosphere, 2008, 70, 1699	China	79	1951	3.7	2.3	6			0.4		Marine
Kim	Journal of Hazardous Materials, 2008, 154, 756	South Korea	35–40	1961-1954	50	22	72				2.11	Marine
Hashimoto	Marine Pollution Bulletin, 1995, 30, 341	Pacific Ocean	1050–1080		2	nd						Marine
Yao	Environ. Toxicol. Chem., 2002, 21, 991	Japan	55–58	1937	520	100	620			4.2		Marine (Tokyo Bay)

Table 8.2. Preliminary table of concentrations of dioxins in archived soils

AUTHOR	REFERENCE	LOCATION	SOIL DEPTH	AGE	PCDD	PCDF	PCDD/F	TEQ-PCDD	TEQ-PCDF	TEQ-PCDD/F	TOC	COMMENTS
					PG/G D.W		PG/G D.W	PGTEQ/G D.W	PGTEQ/G D.W			
Green	Environ. Sci. Technol., 2004, 38, 715	India	surface	1914	7	22	29					Soil
		USA	surface	< 1900	412	58	470					Soil
		Canada	surface	< 1900	2	4	6					Soil
		Canada	surface	< 1900	63	20	83					Soil
		Africa	surface	< 1900	1273	77	1350					Soil
		UK	core	< 1900	5-520	2-15					0.09-0.46	Soil

9 Report on progress of Cooperative Research report on sediment dynamics

WGMS takes note that the paper on Sediment Dynamic has been finalized and edited along 2008. WGMS suggests dealing with this paper at the next meeting with the objective of extracting recommendations for considering sediment dynamic in the assessment of monitoring data. Furthermore, the Group proposed to update the paper and to add further chapters on other regions after approximately 5 years or earlier if any new results of importance arise. For example, the influence of climate change on sediment dynamics may be considered as is already done for the Baltic region.

10 Report ongoing and new projects involving passive sampling:

10.1 Claire Mason presented an introduction to the use of gel technology in passive sampling on behalf of Ruth Parker (Cefas), Gary Fones (SEES, University of Portsmouth) and Lorna Teal (OceanLab, Aberdeen University).

Through a NERC knowledge transfer grant (Fones) and a joint funded PhD studentship between Cefas and Aberdeen University a collaboration has been undertaken to examine the utility of gel technologies to R&D and monitoring applications and linking Sediment Profile Imagery (SPI) with gel sampling capabilities.

In the past, DGT (Diffusive Gradients in Thin Films) and DET (Diffusive Equilibration in Thin Films) in-situ techniques for the measurement of metals in marine and fresh water sediment have been applied in numerous locations and sediment types. These gel techniques were first developed by Zhang and Davison (1994) but their application in the marine environment and especially sediments has been very limited (e.g. Fones, G, 2001, 2004).

A primary aim of the collaboration has been using novel in-situ techniques for linking biological activity to sediment function using DGT alongside Sediment Profile Imagery (SPI). SPI is a fast method spatially of measuring impact in the marine environment but needs a real chemical measurement of the aRPD (apparent Redox Potential Discontinuity) to be confident in the interpretation of the colour changes visualised in the SPI image. Measurements from the DGT gels will enable profiles of iron and manganese to be measured against the apparent image aRPD. Colouration of Fe phases provides basis for qualitative relationship between sediment colour and redox state. Therefore the depth of colour measured in the sediment core can be used as a proxy for sediment function. This approach has been tested by making simultaneous in-situ high-resolution measurements of biological activity and sediment redox conditions using the SPI camera at North Dogger (80m, muddy sand) and Oyster Ground (~40m, muddy sand, high bioturbation). The DGT gel plates were added onto the front of the face plate of the SPI camera. The profiles measured from the DGT for various metals were very similar for both the Dogger Bank and Oyster Ground. However, a segmented regression combining Fe and Mn profiles provides an indication of the Fe redox boundary. When compared with the aRPD boundary on the SPI image, the DGT determined Fe redox boundary matched well at the Oyster ground, but at the Dogger was ~5cm deeper for the Fe redox boundary measured by DGT than shown on the image. This is believed to be because high sulphate reduc-

tion rates at the Dogger leads to formation of FeS which prevents free Fe ions being available for uptake by the DGT at Dogger Bank.

The plan this year is to learn from the results of all of these studies and develop bespoke methodology to analyse these gels and promote their use in future monitoring programmes, in particular at disposal sites. An update of progress will be reported to the WGMS next year.

Davison, W., and Zhang, H. 1994. *In situ* speciation measurement of trace components in natural waters using thin-film gels. *Nature*, 367: 545–548.

Fones, G. R., Davison, W., Holby, O., Jørgensen, B. B., and Thamdrup B. 2001. High-resolution metal gradients measured by in situ DGT/DET deployment in Black Sea sediments using an autonomous benthic lander. *Limnology and Oceanography*, 46(4): 982–988.

Fones, G. R., Davison, W., and Grime, G.W. Development of constrained DET for measurements of dissolved iron in surface sediments at sub-mm resolution, *Sci. Total Environ*, 221 (1998): 127–137.

10.2 Freely dissolved concentrations of polycyclic aromatic hydrocarbons and chlorinated biphenyls in the Clyde estuary, Scotland

Ian Davies made a short presentation of work carried out at FRS by Laura Abbott as part of her MSc project.

Passive sampling using a single reference phase that equilibrates with the dissolved concentration in the sampling medium has been shown to be an attractive mechanism of studying the availability of contaminants in water and monitoring the concentrations of persistent pollutants such as polycyclic aromatic hydrocarbons (PAHs) and chlorinated biphenyls (CBs).

The FRS Marine Laboratory undertook a field study from April to June 2008 utilising silicone rubber strips as passive samplers for freely dissolved PAHs and CBs at thirteen sampling sites from fully marine to freshwater areas of the River Clyde estuary and Firth, Scotland. The Clyde is one of Scotland's most contaminated large estuaries due to current and historical industrial activities and domestic waste inputs. The survey areas are used for a range of marine activities, including shipbuilding and repair, ferry terminals, yachting and marinas, and are subjected to discharges from sewage treatment works upstream.

Silicone rubber sheets were pre-cleaned, pre-spiked with some deuterated PAHs and CBs used as performance reference compounds, and deployed in 6 different locations (outer estuary) and 7 inner sites within the Clyde River at depths of 1.5 to 2m below the water surface to accumulate PAHs and CBs. After 6 weeks exposure, samplers were retrieved, cleaned of any fouling and extracted for the determination of PAHs and CBs by GC-MS and GC-ECD, respectively.

The sampling rates, calculated by iteration with log silicone rubber-water partition coefficients ranged from 1.4–12.9 L day⁻¹ at the different stations, were used to calculate the freely dissolved concentrations of 32 individual PAHs and 28 CBs.

The total freely dissolved concentrations of PAHs generally decreased seawards in the estuarine part of the transect from 285 ng L⁻¹ to 25 ng L⁻¹ in the fully marine areas. Intermediate concentrations were found in the freshwater parts of the transect. Higher concentrations were found associated with industrially active or impacted sites and urban locations, particularly for the lighter PAHs (e.g. naphthalene and al-

kylated homologues). Systematic differences in the distributions of PAHs between sites suggest the influence of mixed sources of PAHs in the survey area, for example including petrogenic sources of contamination associated with industrial activity at some of these locations.

The total freely dissolved concentrations of CBs ranged from 0.97 ng L⁻¹ at a fresh water sampling site to 5.43 ng L⁻¹ at a ferry pier close to a naval base. High total dissolved concentrations were also seen at other industrial sites, including a shipyard and harbours. Concentrations at the fully marine sites were intermediate between those at the industrial and freshwater sites. Systematic differences through the transect were found in the patterns of CB congeners, suggesting sources with different congener ratios within the transect.

The results from this survey confirm that silicone rubber passive samplers can be successfully used in monitoring programmes for hydrophobic contaminants in water of fresh to fully marine salinities.

10.3 Partition coefficients and the bioavailability of polycyclic aromatic hydrocarbons (PAHs) in marine sediments affected by discharges from aluminium smelters

Ian Davies made a short presentation of work carried out at FRS by Kyari Yates.

The availability of polycyclic aromatic hydrocarbons (PAHs) in sediment for uptake by organisms has been addressed through equilibrium partition theory, and linked to the freely dissolved concentrations in sediment pore waters. The pore water concentration is important in the assessment of biological effects as only dissolved concentrations tend to partition into biological membranes. The knowledge of concentrations in sediment pore water and the partitioning behaviour between solid and dissolved components of the sediment of contaminants such as PAHs is therefore necessary to improve environmental risk assessment which is currently commonly based on generic estimates of these partition coefficients.

Silicone rubber passive samplers have been used in experiments at FRS Marine Laboratory to provide estimates of the free dissolved concentrations of PAHs in sediment pore water and site-specific sediment-water partition coefficients. Sediment samples were collected in Loch Leven (Scotland) and Vefsn fjord (Norway), both of which have been affected by discharges from aluminium smelting. Freely dissolved pore water concentrations and sediment-water partition coefficients were determined using the silicone rubber passive sampling method. Briefly, wet sediment samples were kept in contact with pre-cleaned silicone rubber sheets by shaking for 20 days in a light and temperature controlled room in different phase ratios (0.007–0.18 g silicone rubber per g of sediment). After this time, the sheets were Soxhlet extracted and PAHs were then analysed by gas chromatography with mass selective detection.

The total freely dissolved concentrations of 31 PAHs in pore water in sediments collected from around smelters in Scotland and Norway ranged between 21 and 543 ng L⁻¹. Concentrations in the sediment pore water in Vefsn fjord were always higher than in Loch Leven, although sediments in the first location showed higher total PAH concentrations.

The available proportions of PAHs in the sediment generally increased with molecular weight.

Median values of log calculated from the application of the silicone rubber samplers were compared across the sampling areas. Significant positive linear correlations between $\log K_{oc}$ and $\log K_{ow}$ were obtained for all the sediments. The generally positive deviations of $\log K_{oc}$ above $\log K_{ow}$ indicate that the PAHs are more tightly bound to the sediments than suggested by $\log K_{ow}$ values, and less available to take part in exchanges with sediment-dwelling organisms. At low ring numbers, the Vefsn site showed the greatest positive deviation from expected log values, followed by the Leven site. These deviations from the values expected in the smelter impacted sites (Leven and Vefsn) may be a result of the presence of high molecular weight aromatic components within the smelter waste, which has been linked to the strong binding of PAHs in such sediments.

10.4 The INRAM project

Patrick Roose presented preliminary results of the INRAM project to the group that showed how the use of passive samplers for chemical monitoring can be combined with ecotoxicological monitoring

INRAM is a 4-year project called (Integrated Risk Assessment and Monitoring of micropollutants in the Belgian coastal zone) financed by the Belgian Federal Science Policy Office, and aims to assess in an integrated approach the risks of micropollutants to the Belgian coastal zone ecosystems and man. Passive sampling will be used as an innovative approach to measure contaminant pressure in the environment. During the project, a large group of hydrophobic organics is being measured at nine sampling points with passive samplers. Passive sampling is also be used as a tool for in lab toxicity tests at constant and environmentally relevant concentrations

The first deployment of samplers has been completed and the results are being processed. The initial investigation focussed on low molecular PAHs, for which equilibrium was reached during deployment. The concentrations in the sheets, expressed as ng/g, were recalculated to C_w (ng/l). This is the freely dissolved concentration and also assumed to be the fraction of analytes that is directly bioavailable (Smedes and Koning, 2007). This concentration can therefore be considered as an indicator for toxicant pressure on the ecosystem. For the sum of the low molecular PAHs, the freely dissolved concentration varied from 2 ng/l at NP2' to 29 ng/l at OO2. Considering that this is an integrated concentration covering a period of 6 weeks, it is hardly comparable to the whole water concentration of these compounds calculated from point sampling (Smedes *et al.*, 2007a; Smedes *et al.*, 2007b). Higher concentrations during the two sampling occasions with conventional methods suggested a more polluted situation that was contradicted by the results of passive sampling. The preliminary results suggest therefore that passive sampling gives a better estimate of the actual contaminant pressure in the water.

A series of ecotoxicological tests have been performed in which test organisms were exposed to mixtures desorbed from passive samplers. The results for the 72h growth inhibition test with the marine diatom *Phaeodactylum tricornutum* were presented to the group. This test was repeated three times and an excellent reproducibility was found. Samples collected at a specific station in the harbour of Oostende, consistently showed a significant growth inhibition. In another series of tests, passive sampler were used for the 24h larval development test with *Crassostrea gigas* (see annual report of 2007) and a 7 day cellular energy allocation assay with *Mytilus edulis*. The oyster test showed remarkable percentages of dead or abnormal individuals that could

only partially be explained by the results from the chemical analysis. However, the station that showed the worst chemical situation invariably showed the most pronounced effects. Work on this will continue in the coming 2 years and more results should be available by next year.

Smedes, F., and Koning K. 2005. Passive sampling of hydrophobic contaminants with silicone rubber in concert with deployed mussels. Evaluation of 3 years monitoring in Dutch Marine waters. Presentation on the Passive Sampling Training Workshop, 27 June–6 July 2005 RIKZ-Haren, The Netherlands.

Smedes, F., Davies I. M., and Tronczynski, J. 2007a. ICES Passive sampling trial survey for water and sediment (PSTS) 2006–2007. Part 1: Objectives, Design and Realization. International Council for the Exploration of the Sea, Annual Science Conference, 2007, Helsinki, Finland. ICES CM 2007/J:02.

Smedes, F., Van der Zande, T., Roose, P., and Davies I. M. 2007b. ICES Passive sampling trial survey for water and sediment (PSTS) 2006–2007. Part 3: Preliminary interpretation of field data. International Council for the Exploration of the Sea, Annual Science Conference, 2007, Helsinki, Finland. ICES CM 2007/J:04.

10.5 The use of passive samplers for polar pesticides

In 2007 the NERI and the Environmental Center of Ringkøbing used POCIS passive samplers to collect polar substances in Nisum Fjord (Dahllöf, 2008). The project documented the presence of 12 herbicides and 8 degradation products, including the now forbidden Atrazine, 4-nitrophenol, BAM, DNOC and isoproturon. The aim of the project was to investigate if herbicides could be found, that could explain the lack of eelgrass recolonisation of Nisum Fjord. No calibration of the samplers was performed, but using freshwater uptake rates, rough estimates of diuron and isoproturon concentrations was obtained, indicating levels previously shown to have effects on growth of eelgrass in combination studies.

A new project involving POCIS samplers in combination with silicone rubbers are planned for 2009, to investigate endocrine disrupters in Danish streams. It will be combined with investigation of biological effects in caged freshwater mussels at the same positions as the passive samplers, and in vitro tests on mammalian cells from extracts of the passive samplers. Analyses of the passive samplers include phthalates, phenols, PFAS, organotin, pesticides and estrogenic substances.

Dahllöf, I., Mogensen, B. B., Bossi, R., and Jensen, I. 2008. Arbejdsrapport fra DMU nr. 244.: Forekomst af herbicider i Nisum Fjord. Danmarks Miljøundersøgelser, Aarhus Universitet. 21 s. (in Danish).

11 Technical annex to the JAMP Guidelines for monitoring of dioxins in sediments, taking into account advice from SIME 2007

In 1998 OSPAR listed polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF) as a group of chemicals for priority action. Following the decision process within OSPAR it was decided to include them in OSPAR monitoring. For this monitoring SIME advised that monitoring of dioxins sediments should only be carried out in specific areas (such as sedimentation areas or estuaries) because of time lag (10–12 years) in deposition of quantities required for sampling. In support to monitoring of dioxins and furans in sediment OSPAR request ICES to prepare a technical Annex to the JAMP guidelines for Monitoring of Contaminants in Sediment, giving guidance on the analyses of these compounds.

At the meeting work continued on the first draft, prepared by Eppe Gauthier (Belgium). As it stands, the draft provides some advice on the main steps of the analytical procedure to determine PCDDs and PCDFs in marine sediments. It is mainly based on EPA Method 1613 B (US EPA, Method 1613 Revision B, 1994) that seems to be the most generally accepted method by labs involved with dioxin analysis.

This document needs to be completed/reviewed by experts intersessionally to obtain a more advance draft together with the MCWG.

12 Technical annex to the JAMP Guidelines for monitoring of monitoring of PFOS in sediments

WGMS is collaborating with MCWG on this topic and MCWG has agreed to take the lead. It is expected that a draft will be made available at MCWG 2009 with the aim to finalise the document after review by both groups in 2010.

13 Technical annex to the JAMP Guidelines for monitoring of chlorinated biphenyls in sediment to ensure that they are adequate for monitoring of planar CBs in this compartment

The WGMS 2008 agreed on the need of adding some coplanar PCBs (i.e. certain non-ortho- and mono-ortho PCBs, which exhibit a dioxin-like toxicity) to the list of those already being analysed in the monitoring programs of the OSPAR area. Since these congeners are usually present at very low concentration, their analysis requires specialised fractionation procedures and very low detection limits. Therefore the Technical Annex 2 to the JAMP guidelines for monitoring chlorinated biphenyls in sediments was amended. Patrick Roose has revised and updated the existing version with the aim to ensure that the guidelines are adequate also for the analysis of these congeners. The sections which have been revised are those related to clean-up, detection by GC-MS and quality assurance/quality control.

The final draft of the revised version of the guidelines will be submitted first to Lynda Webster (FRS Marine Laboratory, Aberdeen, UK) and subsequently to the MCWG 2009 for critical review. Afterwards, the guidelines can be finalised intersessionally by both groups.

14 Update of JAMP guidance on normalisation of contaminant concentrations in sediment

14.1 Background¹

The purposes of the OSPAR JAMP Guidelines for Monitoring Contaminants in Sediment is to address OSPAR objectives for hazardous substances in Convention waters, namely:

¹ This topic was introduced with presentations by Foppe Smedes and Ingemar Cato. A short summary of their presentations can be found in Annex 3 and 4.

- Preventing pollution of the maritime area by continuously reducing discharges, emissions and losses of hazardous substances, with the ultimate aim of achieving concentrations in the marine environment near background values for naturally occurring substances and close to zero for man-made synthetic substances, and that
- Hazardous substances should not give rise to unexpected or unacceptable biological effects.

Environmental monitoring is carried out, and monitoring data have been used to address these objectives. Studies of temporal trends in concentrations express the environmental response to control measures applied to inputs of contaminants to the sea and to assess progress towards background concentrations. Comparisons of observed concentrations with Background Concentrations (BCs) through the use of Background Assessment Concentrations (BACs) are used to determine whether concentrations are at or close to background. Comparisons of observed concentrations with OSPAR Environmental Assessment Criteria (EACs) or similar assessment criteria are used to indicate whether concentrations are at levels that are not expected to give rise to unacceptable biological effects.

Normalisation of the concentrations of contaminants in sediments is described in the current Annex on normalisation in the JAMP Guidelines for Monitoring Contaminants in Sediment as a procedure to correct contaminant concentrations for the influence of the natural variability in sediment composition (grain size, organic matter and mineralogy).

The need for normalisation arises from the observation that most natural and anthropogenic substances (metals and organic contaminants) show a much higher affinity to fine-grained particulate matter than to the coarse fraction. Constituents such as organic matter and clay minerals show the strongest adsorption capacity for contaminants.

A consequence of this affinity is that it is commonly found that, if the pollution level is constant, there is a correlation between the concentration of contaminants and cofactors that act as proxies for the phase or phases in the sediment which show high affinity for the contaminants. For example, in sediment samples that are in equilibrium with the same water, the concentrations of organic contaminants such as PAHs or CBs can show correlations with the concentration of organic carbon. This is conceptualised as indicating that organic matter shows a high affinity for these substances, and that organic carbon acts as a proxy for organic matter. It should be noted that the nature of organic matter can differ between samples (in space and time) and that therefore its affinity for contaminants can also vary. Some workers have used organic nitrogen in the same way.

In the case of metals such as lead, cadmium and mercury, good correlations with the concentrations of aluminium and lithium have been reported, conceptualised as indicating that these elements are primarily associated with clay minerals. However, the situation is less clear-cut than for organic contaminants in that good correlations with organic carbon have also been reported. In some cases, this may indicate that the metals are also associated with organic matter, but the situation is complicated by correlations between the concentrations of aluminium and TOC or % fine-grained material in the sediment, for example.

The linear correlations found between concentrations of contaminants and cofactors such as aluminium, lithium or organic carbon or expressions of grain size is the basis

of normalisation procedures that have been used to aid the interpretation of monitoring data in OSPAR programmes (Figure 14.1). If normalisation is not applied, the variations in bulk sediment properties add to the overall variance in the contaminant data, and in some cases can be a dominant source of variation. Patterns of concentrations within time series, or in spatial surveys in small geographical areas can largely reflect differences in particle size distribution between samples, and can reduce the power of monitoring programmes to address the objectives of the JAMP.

The slopes of the correlations between contaminant concentrations and cofactor concentrations are greater in locations/areas where anthropogenic contamination occurs than in areas that can be considered as uncontaminated or background areas. These slopes could be used as an expression of the degree of contamination, but the amount of field and laboratory work required to establish the correlations routinely in monitoring programme would be very high, and therefore advantage has been taken of the common expected linear correlations to make use of the ratios between contaminant and normaliser concentrations as a measure of the slope (taking account of the concentrations in non clay materials present in the sample).

Expression of the outcome of normalisation as the slope of the correlation between contaminants and normalisers results in concentrations of contaminants in sediment being expressed in unfamiliar units. For presentational reasons therefore, so that the normalised concentrations are expressed in more familiar units, normalised concentrations have been expressed as the equivalent concentrations that would be found in sediment of the same degree of contamination but of a standard composition, typically representing a high proportion of fine grained material. This has been approximated as equivalent to concentrations of 5% aluminium, 50 ppm lithium, or 2.5% organic carbon, which has previously been found to be an approximate average between typical concentrations in sieved fractions of <63 and <20 μm .

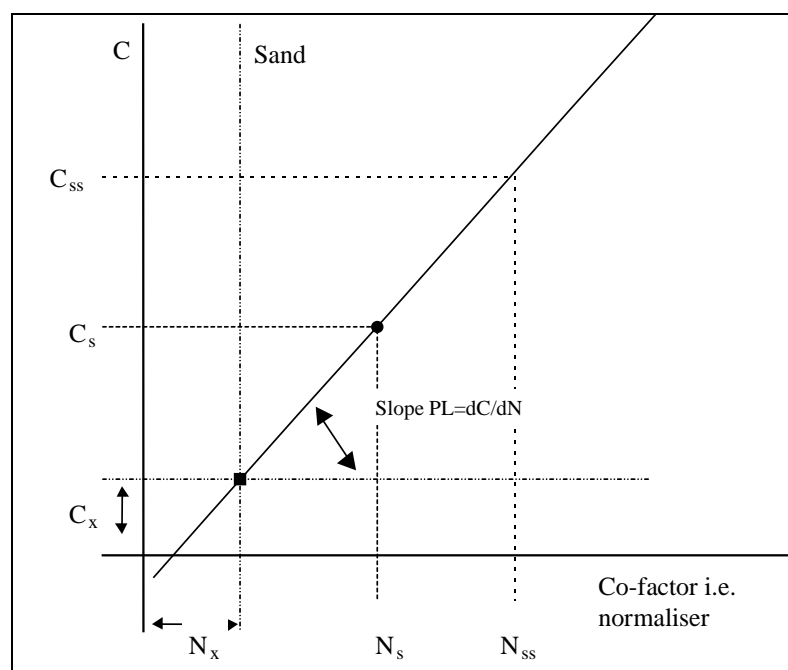


Figure 14.1. Relationship between the contaminant C and the co-factor N (from Smedes et al, 1997).

As discussed in the OSPAR JAMP Guidelines for Monitoring Contaminants in Sediment, the isolation of a fine fraction (e.g. $<20\ \mu\text{m}$, $<63\ \mu\text{m}$) of sediment by sieving can be regarded as a physical normalisation to reduce the differences in granulometric composition between sediment samples, and is applicable to both metals and organic contaminants (Ackermann *et al.*, 1983; Klamer *et al.* 1990). Consequently the coarse particles, which usually do not bind anthropogenic contaminants but generally act to dilute their concentrations, are removed from the sample. The degree of normalisation achieved by sieving is such that it may be possible to directly compare contaminant concentrations measured in these fine fractions. In addition, the differences in sediment composition due to geochemical nature remaining after sieving can be further normalised by the use of co-factors such as aluminium, lithium or TOC. Thus, sieving is a first powerful step in normalisation.

There are a number of practical benefits to monitoring that result from the sieving of sediments prior to analysis. Firstly, the concentrations of both contaminants and geochemical normalisers are greater in the sieved fraction than in the bulk sediment. This can often reduce the uncertainty in the chemical analyses of the sample. This can be particularly important in sediments that are dominated by sand grade material. The concentrations of contaminants in the bulk sediment can be very low and difficult to measure with low uncertainty. This problem is much less significant in analyses of sieved fine fractions.

Secondly, differences in analytical methods, particularly for metals, are less important in the analyses of a sieved fine fraction than in the analysis of whole sediments. The primary difference between analytical methods arises from the use of methods designed to determine the total concentration of metals in a sample (e.g. total digestion methods, or X-ray fluorescence), and those that employ partial digestion methods (e.g. strong acid digestions). The differences are again most important in very sandy sediments. The omission of much of the coarse refractory material that is only susceptible to dissolution by very rigorous methods (e.g. HF digestion) results in there being much smaller differences between the analyses of the sieved fraction by total or partial extraction methods.

Finally, the pivot values have much less importance in the normalisation of analyses of sieved fractions than in the analysis of total ($< 2\text{mm}$) sediment. The importance of accurate knowledge of appropriate pivot values is very greatly reduced by prior sieving of the sediment. Again, this is particularly important in sandy sediments.

14.2 Critical comments rose concerning normalisation

The critical components of the conceptual model of normalisation and its use in relation to OSPAR objectives are:

- a) The existence of useful correlations between contaminant and cofactor concentrations
- b) The degree to which a single set of pivot values, varying only with broad categories of analytical method (e.g. total extraction/digestion methods versus partial strong acid extractions for metals), can be applied across the Convention area
- c) The degree to which a single set of background concentrations (and associated values of normalisers) should be applied across the Convention area
- d) The use of the same normalisers across the Convention area (mainly aluminium of metals and TOC for organics).

Experience of the application of normalisation in OSPAR data assessments has led to all these aspects of normalisation being criticised. WGMS therefore reviewed the bases of the criticisms, and developed proposals for modifications to the way in which normalisation is applied in OSPAR programmes to accommodate, where possible, the criticisms that have been made.

14.2.1 Correlations between contaminants and cofactors

It has been observed in some areas that the correlations between contaminant and cofactor concentrations may be weak or even absent. A number of reasons might give rise to this observation, including that the cofactor used truly inappropriate for the contaminant of concern, that the degree of contamination (environmental quality) is very variable with time or space, or that there is significant additional variance arising from the measurements of the concentration of the chosen cofactor.

The purpose of normalisation is to reduce the variability between samples arising from differences in bulk sediment properties. In the situations outlined above, the use of normalisation would not have the desired effect. WGMS therefore recommend that the decision as to whether to apply normalisation to a time series of data should be based upon the apparent effectiveness of the normalisation. Current procedures applied by OSPAR MON in assessing time series of data involve the application of smoothers or linear regressions (for short time series). An effective normaliser should reduce the residual variance around the fitted smoother or regression. WGMS therefore recommend that normalisation should be applied if this results in a reduction of the residual variance in time series, but should not be applied if the residual variance is not reduced.

14.2.2 Pivot values

Pivot values represent the concentrations of contaminants and cofactors in sediment containing no fine-grained material, i.e. in sand. The concentrations of some cofactors have been found to be zero (undetectable) in sand, for example TOC. Other cofactors, such as aluminium, are commonly present in measureable concentrations in sand (e.g. from inclusion in the sand fraction of minerals other than quartz, for example feldspars), and there can be measureable concentrations of metals in the sand fraction from these minerals or from coatings on sand grains. The degree to which aluminium (for example) is extractable from such minerals is dependent upon the analytical method (chemical extraction/digestion method) used. Strong acid partial digestions will extract less aluminium than a total digestion procedure. Current normalisation procedures used by OSPAR MON takes account of the differences in pivot values between methods.

The main concern expressed regarding pivot values is that the composition of sand-sized material may differ significantly between different parts of the Convention area. The use of inappropriate pivot values could have significant impact on the calculated normalised concentrations, particularly for sediment samples containing relatively small proportions of fine-grained material. WGMS therefore recommend that CPs be invited to present proposals for pivot values appropriate to particular parts of the Convention area. Such regionalised pivot values should be applicable over large parts of the Convention area, for example across entire Regions, or to all monitoring data from a particular country. In the absence of accepted new proposals, the current pivot values with their uncertainties should continue to be used.

14.2.3 Background concentrations

Background Concentrations (and associated Background Assessment Concentrations) are required to address the OSPAR objective that concentrations of hazardous substances should be at or close to background. Background concentrations of man-made synthetic substances, such as PCBs, are zero. However, background concentrations of naturally occurring substances, such as metals and PAHs, need to be defined. This has been done through previous meetings of WGMS and other groups. Generally, they reflect concentrations found in sediment from pre-industrial times from core samples, or from surface sediments in areas considered to be remote from significant anthropogenic inputs of the contaminants of concern.

Two main concerns have been expressed in relation to Background Concentrations. They are both related to the degree to which the current Background Concentrations are appropriate for application throughout the Convention area. Firstly, it has been suggested that the current values, derived from a data set that emphasises the northern part of the Convention area, may not be immediately applicable elsewhere. Secondly, the Background Concentrations are currently expressed as normalised values (to 5% aluminium or 50 ppm lithium for metals and 2.5% TOC for organic contaminants), and it has been suggested that the “reference” values of the cofactors may not be appropriate for all areas. The use of inappropriate values for Background Concentrations could lead to misleading assessments as to whether concentrations in sediment are at or close to background.

WGMS therefore recommend that CPs be invited to present proposals for Background Concentrations and associated cofactor values that they consider to be appropriate to particular parts of the Convention area. The combinations of Background Concentrations and associated cofactor values should be consistent with the way in which pivot values to be used in the assessment of the field data are expressed, to allow the construction of straight lines joining pivot values and Background Concentrations. Such regionalised Background Concentrations should be applicable over large parts of the Convention area, for example across entire Regions, or to all monitoring data from a particular country. In the absence of accepted new proposals, the current Background Concentrations and cofactors should continue to be used.

14.2.4 The same normalisers across the Convention area

The current data assessment methods used by OSPAR MON use aluminium as normaliser for metals and TOC as normaliser for organic contaminants. It has been suggested that this harmonised approach may not be appropriate for all parts of the Convention area. In some areas, it may be that other normalisers may be more effective than Al, Li or TOC for some contaminants. For example, in some areas it might be more effective to use TOC as cofactor for mercury.

WGMS therefore recommend that CPs be invited to present proposals for the specification of cofactors to be used for the normalisation of concentrations of particular contaminants in their monitoring data. The effectiveness of the normalisation would be assessed through the effect of application of normalisation on the residual variance about time series, as described above. When making proposals, it will be necessary for CPs to ensure that pivot values and Background Concentrations expressed in relation to the same normalisers are also available. Such regionalised approaches to specification of cofactors should be applicable over large parts of the Convention area, for example across entire Regions, or to all monitoring data from a particular

country. In the absence of accepted new proposals, the current approach to normalisation should continue to be used.

14.3 Applicability of new pivot values or Background Concentrations

Most of the data currently available to OSPAR assessment groups are from inshore or shelf sea areas. In some parts of the Convention area, the shelf is rather narrow, and monitoring programmes can extend into relatively deep water on the continental slope. The implementation of the EU Marine Strategy Framework Directive, which covers large areas of European Seas beyond the continental shelf is also likely to increase the pressure for survey and monitoring activity in deeper water. WGMS noted that sediments in deep water tend to have different characteristics from those in shallow and inshore areas. WGMS therefore suggested that it might be necessary to define pivot values or BCs applicable different depth zones. WGMS suggest that two depth zones be considered – shelf and inshore areas (including estuaries) in less than 200m water depth, and deep-water sediments in more than 200m depth. WGMS noted that some current sediment monitoring data from Spain (and Portugal) are obtained from water more than 200m deep. As a preparatory step, WGMS recommend that ICES Data Centre be asked to use the information on station location in the Station Dictionary to complete the available data field for depth of water at the sampling station. At present, the database contains a reasonable amount of records for which this information was provided.

14.4 Upper assessment criteria – EACs, etc

The 2008 OSPAR MON assessment of contaminant concentrations in sediment employed two types of assessment criteria. One of these (termed T0 in their report) was used to assess whether concentrations were at or close to background, i.e. the T0 criteria were the Background Assessment Criteria.

The upper type of assessment criteria (termed T1 in their report) were used to assess whether the concentrations observed were below levels that were unlikely to result in unacceptable biological effects. The appropriate OSPAR criteria are EACs, but MON found that EACs were not available for all the contaminants of interest. Specifically, EACs for sediment were available for PCBs but not for metals or PAHs. In order to have a complete set of criteria, MON used ERL values for metals and PAHs. MON expressed the concentrations of all contaminants in normalised form for the purpose of trend assessment, and for comparison with BACs, which are expressed as normalised concentrations. For consistency, MON made comparisons between normalised concentrations and EACs and ERLs. While EACs for PCBs are expressed as concentrations normalised to TOC, ERLs are expressed on a non-normalised basis. It has been argued that comparison of normalised field data with non-normalised ERLs is inappropriate.

The preceding discussion has lead to recommendations that the MON assessment procedure be amended to allow for an increased level of flexibility in normalisation procedures, pivot values and BCs. If this increased flexibility is acceptable to ICES/OSPAR, it may also be appropriate to revisit the current assessment procedure against EACs/ERLs with a view to introducing a parallel degree of flexibility in the expression and testing of data against these T1 criteria.

14.5 The role of passive samplers

In the present normalisation procedures used by OSPAR MON in assessing CEMP data on contaminants in sediment, the concentrations of organic contaminants are expressed normalised to organic carbon. Organic carbon is a representative parameter for organic matter, as this is the phase in the sediment that is mainly responsible for the affinity or uptake capacity of the sediment for organic contaminants. Contaminant concentrations expressed on organic carbon are expected to be linked to the concentration in the aqueous phase (sediment pore water) through the water-organic carbon- partition coefficient. In that way, the normalized concentrations are an index of the concentrations that are available for transport or uptake by organisms.

Expressing contaminant concentrations on organic carbon is essentially the ratio between the concentration of the contaminant and the uptake capacity of the sediment for that contaminant. This ratio is proportional to the thermodynamic chemical activity. Applying concentrations expressed on organic carbon in temporal trend studies assumes that the nature of organic carbon, particularly in terms of uptake capacities for organic contaminants, remains constant in time, and also that it is not related to the grain size distribution of the inorganic components of the sediment. Likewise, spatial comparisons assume that organic matter has the same properties over areas larger than single sampling stations. The variety in reported organic carbon-water partition coefficients suggests that the uptake characteristics of organic matter may show differences. There is a growing evidence that the organic matter in sediments is not only a simple amorphous residue of humic and fulvic substances, but that a wide variety of types of carbonaceous materials, such as soot, coal ("active carbon"-like materials) can be present. This variability is not covered by the current normalization procedure. This is not a sufficient reason to abandon current normalization as the consequences of the variation in the properties of sediment organic matter for comparability between sediment samples is considered to be less than the consequences of differences in bulk properties (TOC concentration) of the sediment. Variation in uptake characteristics of the organic matter limits the effectiveness of normalization but not the need for it.

The assessment of the potential of organic contaminants in sediment to cause unacceptable biological effects is concerned with the toxicity of contaminants in the sediment, and their availability for uptake by organisms. Current normalization techniques, and the use of EACs as assessment criteria, is an indirect way to approach risks. As noted above, there are a number of assumptions implicit in the approach, the reliability of which is not entirely clear. WGMS therefore suggest that a more direct approach to bioavailability could result in a better approach to the toxicity of sediment due to the presence of hydrophobic contaminants in sediment. WGMS suggest that passive sampling offers a potentially significant improvement over current sediment quality assessment methods. .

The definition of (bio)availability by Reichenberg and Mayer² (2006) provides a framework for the new approach. They defined bioavailability by two parameters: "chemical activity" and "accessibility". The chemical activity is a parameter from the

² Reichenberg, F. and Mayer, P. 2006. Two complementary sides of bioavailability: Accessibility and chemical activity of organic contaminants in sediments and soils. *Environmental Toxicology and Chemistry*, 25(5): 1239–1245.

classical chemical thermodynamics, related to the fugacity, and can be seen as the driving force for partition driven uptake and release between different phases. This can be measured directly through passive sampling. A reference phase with known uptake capacities (i.e. known water-sampler partition coefficients) is equilibrated with the sediment sample and the reference phase will attain a chemical activity equal to that of the sediment. Doing so with sediments of different origins allows direct comparison between them, and therefore avoids the uncertainty of the possible differences between the properties of sediment organic matter in time or space. In practice, the results of the passive sampling, used for comparisons between sediments, are expressed as free dissolved concentrations in the water phase, essentially equal to concentrations in pore water.

The other aspect of bioavailability is the accessibility of a contaminant in sediment. This can be expressed as the concentration of a contaminant in the solids that can be released to the water phase. Essentially, it is the capacity of the sediment to maintain the concentration level in the pore water. To measure the accessible concentration, a sediment is mildly extracted through the water phase by a sorbent or passive sampler with excess capacity. Extraction of the sediment continues until the concentration in the water phase becomes negligible. This is a more variable parameter than the freely dissolved concentration in pore water as the endpoint may vary with the methodology used. Furthermore, the result is related to the proportion of fines and/or organic matter in the sediment sample. In other words, two samples with the same concentration in the pore water can have different accessible concentrations depending on whether the sediment is sandy or muddy.

Passive sampling techniques for sediment are still in development. Most advanced is the measurement of concentrations in pore water. Various different methods are available that appear to show useful results, but time is still needed to show the comparability and improve the robustness of both the measurement and the assessment methods. Methods are applicable for all types of sediment, although totally sandy sediment can present difficulties. Within the ICES passive sampling trial survey PAHs and PCBs could be measured for all investigated stations³. All participants using the same method allowed direct comparison of obtained concentrations in pore water. WGMS prepared a first set of guidelines for the measurement of concentrations in pore water that used silicon rubber (PDMS) as reference phase.

For accessibility the available methods is more divers giving variable results. Also the focus of methods are different. Extractions with sorbents mainly separate the sediment concentration in their desorption rate. Another method record and desorption isotherm and use the relation of the concentration in the pore water and that extracted from the sediment to find the accessible concentration. Compared to the measurement of the pore water concentration only the methods for accessibility are more operationally defined.

More work is needed to develop and standardize these methods in concert with procedures to assess the results.

³ Smedes, F., van der Zande, A., et al. ICES passive sampling trial survey for water and sediment (PSTS) 2006–2007. Part 3: preliminary interpretation of field data, Helsinki, 17–21 September 2007.

On the basis of that:

- WGMS recommends that where possible CPs should start building experience with monitoring porewater concentrations
- Further investigate methods that will give information on the accessibility

The temperature methaphor

If calories would be a contaminant, chemical activity is as the temperature. Temperature is also the driving force for calories to move and tells if you will burn your fingers. The accessibility is the amount of "available" calories. Accessibility relates to the amount of calories causing that temperature. You will burn your fingers in water of 100°C but not touching polystyrene of the same temperature.

14.6 Draft guidelines

During the meeting work on a new draft guideline was initiated and finalised in the weeks following the meeting. The draft technical annex that resulted from the work can be found in annex 5. WGMS recommends that the draft technical annex is forwarded to OSPAR for approval.

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

No questions were submitted to group.

16 Any other business

No specific issues were raised under this topic but Ingemar Cato gave two informative presentations. A short summery of these is given below.

16.1 Previously dispersed and later banned chemicals

Ingemar Cato gave also presentation on previously dispersed and later banned chemicals in the Skagerrak and Baltic Sea areas, which still pose a threat on the marine environment. Since the 1970s and onwards the use of a number of chemical substances have been banned e.g. mercury, several pesticides as DDTs, Chlordanes, HCHs and organotins (TBT, TFT etc), but still you find them in the most recent accumulated sediments which indicate leaching from contaminated land spots, redeposition of older reworked contaminated sediment or leaches from previously dumped barrels. In the presentation Ingemar gave several examples of these contaminants as well as examples of dumped wastes, e.g. the 23,000 barrels that were legally dumped at international water in the Bothnian Sea by a Swedish chemical company between 1956 and 1964.

The barrels contain industrial wastes. The waste constitutes a catalytic substance, containing mercury chloride, which has been used in the manufacturing of PVC. In total about 9 tonnes of mercury were dumped. The catalytic mercury-containing substance was mixed with concrete and filled to the barrels. Today, the barrels have rust-holes and "rust bubbles" and the catalytic substance mixed with the concrete is visible in the holes. Due to the carbonate undersaturation in the Bothnian Sea the con-

crete is chemical weathered and thus leaching mercury. Aquarium tests of the crete show leaching of mercury and strong accumulation of mercury in the fishes.

Other examples given in the presentation were the sites of dumped chemical weapons, which never came to use during the second World-war. About 300 000 tonnes were dumped by UK, US and the former Soviet Union in the Skagerrak and Baltic Seas. However, the threat to the environment is small as the substances leaching from the weapons will be hydrolysed to not dangerous substances.

Ingemar raised the following question: How many similar dumping sites exist within the HELCOM/OSPAR areas? He concluded that this is an urgent matter to find out, and the importance to locate such sites and to determine and evaluate the risk they play to the marine environment, i.e. which of the dumped chemicals can be considered as running time bombs. Finally, he said that an action plan is needed to clear out all this.

Ingemar also showed the results of an investigation he has carried out between 2003 and 2006 regarding the organotin compounds in sediments of Swedish harbours, marinas, coastal areas and offshore areas of the Swedish waters and EEZ. Despite these chemicals were banned in 1989 and 1993 to be used as antifouling paints on boats <25 m and vessels >25 m length respectively, they still occur in high concentrations (up to 12 000 µg/kg dry m.) in the recent accumulated sediments. Furthermore, investigations show highly developed imposex on gastropods in the contaminated areas. Ingemar concluded that "Organotin compounds are one of the most harmful substances ever dispersed by man to the marine environment - comparable to dioxins and furans".

16.2 Swedish National Status and Trend Monitoring Program for contaminants in marine sediments

The net of sampling stations, the methods used and how the station were chosen in the National Swedish Status and Trend Monitoring Program (NSSTMP) for contaminants in marine sediments of offshore areas were presented by Ingemar Cato. The Programme was launched in 2003 and is sampled every fifth year (last time in 2008). About 150 elements and organic substances are analysed in the topmost sediment (0-1 cm) in these especially selected areas with a continuous accumulation of fine-grained sediments. To achieve a statistical acceptable material seven sites are cored within each of the 16 stations used in the programme. At each site 9 cores is taken. The average accumulation rate at each station is determined by gamma-spechtrometry in order to find the ¹³⁷Cs peak (due to the Tjernobyl accident in 1986), which now acts as a marker for that year in the sediment. The quality of the cores is prior to the subsampling examined with a digital sediment-scanner where a flat x-ray beam scans the core in order to detect disturbances as e.g. bioturbation, anchor tracks. This radiographic examination has been found to be of utmost importance as the sampling is the most critical part in sediment studies.

Finally, Ingemar demonstrated the web-based map service of the Swedish Programme (NSSTMP) where all information and results from each station can be viewed and the data downloaded for free. The Geological Survey of Sweden (SGU) is the data host for elements and organic pollutants in sediments in Swedish waters and EEZ. The Survey has built a new type of database for this and a database open for future new chemicals. In the database also data from regional sediment monitoring programmes and recipient control are loaded. The web-service can be found at SGU's web at the following address:

<http://www.sgu.se/sgu/sv/samhalle/miljo/miljoovervakning/datavard-sediment.html>

17 Recommendations and Action list

The Actions are listed in Annex 6 and the Recommendations in Annex 8.

18 Chair(s) for 2010

In 2008, Patrick Roose was appointed as Chair of the working group with Lucía Viñas as co-chair in order to divide the workload. Given the fact that ICES EG chairmanship is a three year term and both chairs are willing to continue, chairmanship should continue as it is for 2009–2010.

19 Date and venue of the next meeting

Maria Jesus Belunce was kind enough to invite the group to her institute AZTI in San Sebastian, Spain, for their 2010 meeting.

20 Closure of the meeting

The meeting was closed on Friday the 6 March at 13:30. Both Chairs thanked the group for their collaboration to a successful meeting and thanked, on behalf of the entire group, Linda Tyrrell and her colleagues for hosting the meeting in such an outstanding way.

Annex 1: List of participants

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Annex 2: WGMS Agenda

The 29th meeting of the ICES Working Group on Marine Sediments in relation to Pollution Galway (Ireland), 2–6 March 2009

Acting Chairs: Patrick Roose and Lucia Viñas.

Start at 2nd of March at 9h00 (all meeting days).

Closure of the meeting is foreseen at 17:00, 6 March

Item	ToR	Subject
1		a) Opening of the meeting, b) Reflections on the changes in the ICES advisory and scientific proces
2		Adoption of the agenda Arrangements for a working schedule and appointment of rapporteurs Recall actions and Recommendations Sediment Monitoring
3	a	Review and comment on the report of the data assessment from the 2008 meeting of OSPAR/MON in relation to sediments
4	f	Review developments in the use of QUASIMEME information in the interpretation of field data on the ratios of contaminant concentrations
5	g	Review and report on a survey of metals in North Sea sediments in relation to Background Concentrations carried out by Germany
6		Review new developments at the EC level on the development of guidelines for monitoring of sediments in relation to the water framework directive Background concentrations
7	b-i	Investigate if the proposed background concentrations of alkylated PAHs in sediment need to be updated in the light of this assessment and new data supplied intersessionally. Alkylated PAHs concerned: 1) C1-, C2- and C3-naphthalenes; 2) C1-, C2- and C3-phenanthrenes, and 3) C1-, C2- and C3-dibenzothiophenes, and parent dibenzothiophene
8	b-ii	Continue collection of data and develop background concentrations for dioxins. (OSPAR request 4, 2008); Sediment dynamics
9		Report on progress of cooperative research report Passive Sampling
10	d	Report ongoing and new projects involving passive sampling: Projects that combine biological effects measurements with passive sampling; National projects involving the use of passive samplers; International cooperative projects involving passive sampling, including the ICON project; Developments of monitoring guidelines
11	c-i	Technical annex to the JAMP Guidelines for monitoring of dioxins in sediments, taking into account advice from SIME 2007.
12	c-i	Technical annex to the JAMP Guidelines for monitoring of monitoring of PFOS in sediments

13	c-ii	Technical annex to the JAMP Guidelines for monitoring of of chlorinated biphenyls in sediment to ensure that they are adequate for monitoring of planar CBs in this compartment
		Sediment normalisation
14	h	Update of JAMP guidance on normalisation of contaminant concentrations in sediment
		Miscellaneous
15	e	provide expert knowledge and guidance to ICES Data Centre (possibly via sub-group) as requested
16		Any other business
17		Recommendations and Action list
18		Chair(s) for 2010
19		Date and venue of the next meeting
20		Closure of the meeting
		Intended closure time is Friday 6th of March at 17h00

Annex 3: Normalisation of contaminant contents in sediments and how to test them by Foppe Smedes

As introduction to the normalisation discussion Foppe Smedes showed a brief summary of presentations given at the QUASH conference in 1999.

Sediment monitoring programmes that intend to assess the anthropogenic pressure need to correct contaminant contents for the composition of the sediment. This correction for the grain size composition is referred to as normalisation. Discussions in international bodies did not lead to a consensus on what normalisation method is appropriate. Within QUASH, WGMS and OSPAR-MON a lot of work was done to develop procedures for grain size correction of data.

Generally two approaches are presently applied:

- 1) relating the contaminant content to co factor(s) that represent sediment properties (clay, aluminium, lithium, organic carbon) and
- 2) reducing the variability in the sediment composition by isolating a specific grain size fraction, usually the fine particles (sieving).

In the latter method, the fractions obtained by sieving have still variable compositions, i.e. co factor contents, depending on the origin and the mesh size used for sieving (20 or 63µm). So to be accurate the results need further correction using the cofactor content. To obtain international agreement on normalisation procedures with or without sieving a validation is necessary. The basic test criterion is defined as:

“A normalisation procedure should lead to equal results for sediment samples exposed to and in equilibrium with the same water mass, irrespective of the grain size composition”.

Normally this criterion is tested in areas where fine and coarse-grained sediments coexist. Several examples were presented showing relations between contaminants and cofactors. In addition the normalised results of the total sediment and its sieved fraction should not differ. Zink concentrations from the Western Scheldt in sieved and non-sieved samples were normalised showing no significant differences. In other words contaminant and cofactor should be equally distributed. The ultimate test to compare the distribution of contaminant and cofactors is to sieve the sample in coarse and fine fractions. It was shown that also in this case no significant differences in the results existed. Multiple regression with several cofactor showed that using clay (or its representative Al or Li) and organic carbon together gave slightly better results than using a single cofactor.

Annex 4: Normalisation by Ingemar Cato

Ingemar Cato gave a presentation on the Normalisation procedure for sediment (the Gradient Method) worked out by him in the beginning of the 1970's (Cato 1977). The aim of his work was to follow the trends in the load of metals and nutrients in some coastal areas. One of the areas was a fjord where he could follow the successively increased metal load due to the establishment of an oil-refinery in the inner fjord. Another area was an estuary where the sewage treatment plant was closed down and where could follow the opposite trend, i.e. a successively decreasing load. He found out that in this type of clay sediments the normalisation to organic carbon worked best. To illustrate the load he used the slope of the linear regression (Fig. 1). Ingemar Cato also showed the response of the macro- and meiofauna to the changes in slopes of the normalised sediment data. In the end of the presentation he showed that normalisation to co-factors only works in restricted areas, e.g. bays, estuaries and fjords. This because in a huge sea area, as in his case, the Baltic Sea, the relationship between the contaminant and the co-factor is made of huge number of relationships with different loads.

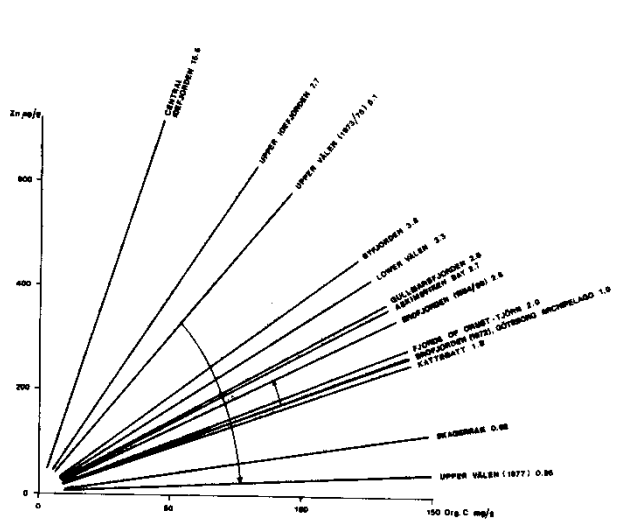


Figure 1. Zinc normalized to organic carbon showing the slopes and changes of the slope in different areas of the Skagerrak Coast of Sweden.

Annex 5: Technical annex on normalisation

Normalisation of contaminant concentrations in sediments

1. Introduction

The purposes of the OSPAR JAMP Guidelines for Monitoring Contaminants in Sediment is to address OSPAR objectives for hazardous substances in Convention waters, namely:

- Preventing pollution of the maritime area by continuously reducing discharges, emissions and losses of hazardous substances, with the ultimate aim of achieving concentrations in the marine environment near background values for naturally occurring substances and close to zero for man-made synthetic substances, and that
- Hazardous substances should not give rise to unexpected or unacceptable biological effects.

Environmental monitoring is carried out, and monitoring data have been used to address these objectives. Studies of temporal trends in concentrations express the environmental response to control measures applied to inputs of contaminants to the sea and to assess progress towards background concentrations. Comparisons of observed concentrations with Background Concentrations (BCs) through the use of Background Assessment Concentrations (BACs) are used to determine whether concentrations are at or close to background. Comparisons of observed concentrations with OSPAR Environmental Assessment Criteria (EACs) or similar assessment criteria are used to indicate whether concentrations are at levels that are not expected to give rise to unacceptable biological effects. Monitoring for spatial distributions is discussed in Section 11 below.

As contaminant concentrations may vary due to differences in bulk sediment composition (e.g. differences in particle size distribution, organic matter content), results from comparisons of observed data to assessment criteria or trend assessments may be obscured. In order to reduce variances of contaminant concentrations due to differences in bulk sediment composition and to increase the power of monitoring programmes to address the objectives of the JAMP, procedures for normalisation of the concentrations of contaminants in sediment have been developed and used in OSPAR assessments of monitoring data.

Taking into consideration experience of the application of normalisation in OSPAR data assessments and the current objectives of the OSPAR JAMP, Technical Annex 5 has been updated/revised.

2. Purposes

This annex provides guidance on the application of methods to normalise contaminant concentrations in sediments. Normalisation is defined here as a procedure to correct contaminant concentrations for the influence of the natural variability in sediment composition (grain size, organic matter and mineralogy). Most natural and anthropogenic substances (metals and organic contaminants) show a much higher affinity to fine particulate matter compared to the coarse fraction. Constituents such as organic matter and clay minerals contribute to the affinity to contaminants in this fine material.

Fine material (inorganic and organic) and associated contaminants are preferentially deposited in areas of low hydrodynamic energy, while in areas of higher energy, fine particulate matter is mixed with coarser sediment particles which are generally have weaker binding capacity for contaminants. This dilution effect will cause lower and variable contaminant concentrations in the resulting sediment. Obviously, grain size and organic matter are important factors controlling the distribution of natural and anthropogenic components in sediments. It is, therefore, essential to normalise for the effects of grain size or organic carbon in order to provide a basis for reliable assessments of temporal trends and for meaningful comparisons of the occurrence of substances in sediments of variable bulk properties with background (assessment) criteria and environmental assessment criteria derived for a defined sediment composition.

In sediment of varying bulk properties, contaminant concentrations will be closely related to the distribution of fine grained material, and any effects of other sources of contaminants, for example anthropogenic sources, will be at least partly obscured by grain size differences. Also in temporal trend monitoring, differences in sediment bulk properties can obscure trends. If samples have a considerable and constant percentage of fine material, the influence of grain size distribution is of minor importance and may probably be neglected.

3. Normalisation procedures

Two different approaches to correct for variable sediment compositions are widely used:

- a) Isolation of the fine fraction by sieving (e.g. $<20\ \mu\text{m}$, $<63\ \mu\text{m}$) can be regarded as a physical normalisation to reduce the differences in sediment granulometric compositions and is applicable to both metals and organic contaminants (e.g. Ackermann *et al.* 1983; Klamer *et al.* 1990, QUASH, 2000). Consequently the coarse particles, which usually do not bind anthropogenic contaminants and dilute their concentrations, are removed from the sample. Then, contaminant concentrations measured in these fine fractions can be directly compared. Subsequently, the differences in sediment composition due to geochemical nature remaining after sieving can be further corrected for by the use of co-factors. Thus, sieving is a first powerful step in normalisation.
- b) Normalisation can be performed by relating the contaminant concentration with components of the sediment that represents its affinity for contaminants, i.e. binding capacity. Such co-factors are called normalisers (cf. section 4). Normalisation of contaminant concentrations can be performed by linear regression to co-factors (Cato 1977; Smedes, 1997; Smedes et al 1997). Another procedure takes into account that the coarse sediment fraction contains natural metal concentrations in the crystal structure before the normalisation is performed (cf. section 4). Combinations of co-factors, possibly identified from multiple regression analysis, can be used as normalisers;

4. Normalisation with co-factors

- a) The binding capacity of the sediments can be related to the content of fines (primary factor) in the sediments. Normalisation can be achieved by calculating the concentration of a contaminant with respect to a specific grain-size fraction such as $<2\ \mu\text{m}$ (clay fraction), $<20\ \mu\text{m}$ or $<63\ \mu\text{m}$;

- b) As the content of fines is represented by the contents of major elements of the clay fraction such as aluminium (Windom et al. 1989) or an appropriate trace element enriched in that fraction such as lithium (Loring 1991), these can also be used as co-factor (secondary). Both, aluminium and lithium behave conservatively, as they are not significantly affected by, for instance, the early diagenetic processes and strong redox effects frequently observed in sediments. Problems may occur in when the sediment is derived from glacial erosion of igneous rocks, with significant amounts of aluminium present in feldspar minerals contributing to the coarse fraction. In such cases, lithium may be preferable (Loring 1991);
- c) c. Organic matter, usually represented by organic carbon, is the most common co-factor for organic contaminants due to their strong affinity to this sediment component.). In some environments, trace metal concentrations can also be normalised using organic carbon content, especially in surface sediments (Cato 1977). The use of organic carbon as co-factor would require further explanation due to the non-conservative nature of organic matter (cf. below).

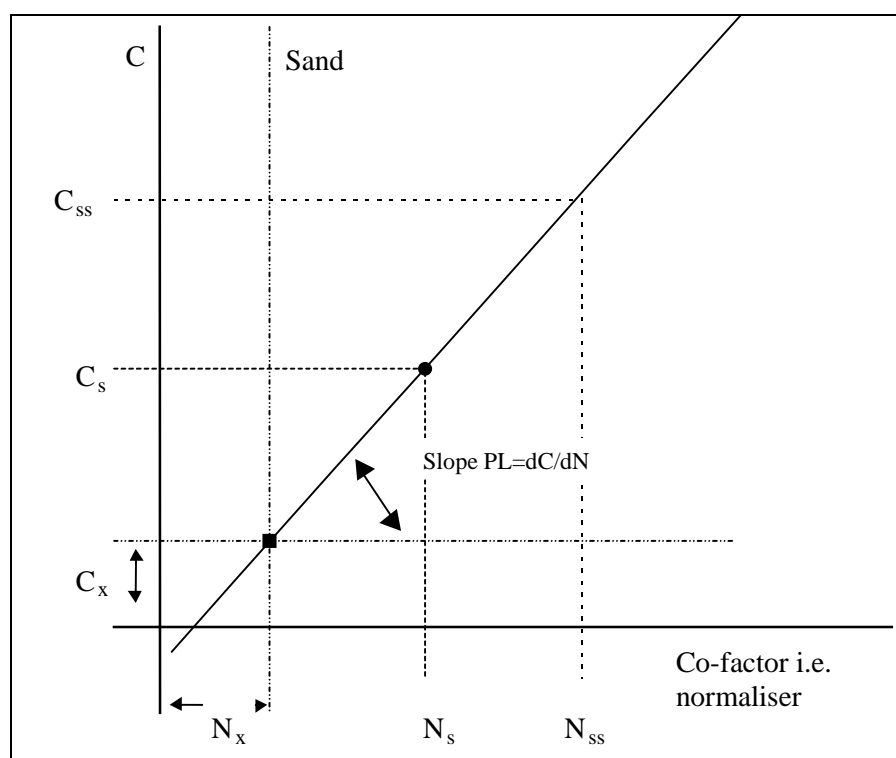


Figure 1. Relationship between the contaminant C and the co-factor N (from Smedes, 1997).

5. Theory

The general model for normalisation taking into account the possible presence of contaminants and co-factors in the coarse material is given in Figure 1 (Cato, 1977; Smedes *et al.* 1997; Kersten and Smedes, 2002). C_x and N_x represent the co-factor and the contaminant contents, respectively, in pure sand. These “intercepts” can be estimated from samples without fines and organic material. The line of regression between the contaminant and co-factor will originate from that point. That means that regression lines of sample sets with a different pollution level and consequently dif-

ferent slopes will have this point in common (i.e. pivot point) (OSPAR 2008). When this pivot point is known only one sample is required to estimate the slope. This allows determination of the contaminant content for any agreed (preselected) co-factor content (N_{ss}) by interpolation or extrapolation. The slope for a sample with a contaminant content C_s and a co-factor content of N_s can be expressed as follows:

$$PL = \frac{dC}{dN} = \frac{C_s - C_x}{N_s - N_x} \quad (1)$$

The extrapolation to an agreed co-factor content, N_{ss} , follows the same slope:

$$PL = \frac{dC}{dN} = \frac{C_s - C_x}{N_s - N_x} = \frac{C_{ss} - C_x}{N_{ss} - N_x} \quad (2)$$

Rewriting gives the contaminant content, C_{ss} , that is normalised to N_{ss} :

$$C_{ss} = (C_s - C_x) \frac{N_{ss} - N_x}{N_s - N_x} + C_x \quad (3)$$

Results of different samples normalised to the agreed N_{ss} can be compared directly.

Normalisation by this model can be applied with different co-factors. Here primary and secondary co-factors can be distinguished. A primary co-factor like the clay fraction or organic carbon is not present in the coarse fraction and consequently has no intercept ($N_x=0$). Al and Li are present in the coarse fraction and therefore are considered to be secondary co-factors. Provided N_x and C_x are known, the model allows recalculation of total samples to a co-factor content usually found in sieved fractions, either <20 or $<63\mu\text{m}$. However such an extrapolation for a coarse grained sample will be associated with a large error due to the uncertainty of the intercepts and the analysed parameters. For a more fine grained sample, the uncertainty of the normalised result is much lower than for normalisation of a sieved fraction to the agreed co-factor content and will result in a more accurate result. The model presented also applies to the normalisation of organic contaminants using organic carbon but in that case the intercepts N_x and C_x will not differ significantly from zero.

Principally, the result allows comparison of data of total and sieved samples, irrespective the sieving diameter but the error has to be taken into account. Through propagation of errors the standard error of the result can be calculated from the analytical variation and the natural variation of the intercept N_x . (Smedes et al., 2005). Results can therefore always be reported with a standard deviation.

6. Considerations on co-factors

The **clay mineral content** is the most important co-factor for trace metals. In the model above the N_x will be zero for clay and only the intercept due to the content of the trace metal in the coarse fraction (C_x) has to be taken into account. However, current intercomparison exercises do not include this parameter. Presently other parameters such as aluminium or lithium are used to represent the clay content.

The **aluminium** content in the sandy fraction may vary from area to area. For some areas aluminium contents in the sandy fractions are found at the same level as found in the fines (Loring, 1991) and therefore the intercept N_x becomes very high. In equation (3) this implies that the denominator is the result of subtracting two large numbers, that is the normaliser content in the sample (N_s) and the normaliser content in only sand (N_x). Consequently, due to their individual uncertainties, the result has an

extremely high error. Obviously, normalisation with low intercepts is more accurate. Much lower intercepts are found if partial digestion methods are used that digest the clay minerals, but not the coarse minerals. Using partial digestion, the spatial variability of the results of aluminium analyses in the sandy fraction has been found to be much smaller than with total methods. Although normalising concentrations of contaminants in fine grained material will always give more accurate results, an error calculation will identify whether using coarse samples (and total methods, e.g. HF, X-ray fluorescence, lithium tetraborate fusion) allows the requirements of the program to be met.

For most areas the **lithium** content in the sandy fraction is much lower than in the fine fraction. In addition, results from partial digestion and total methods do not differ significantly. There is only little spatial variability of the lithium content in the sandy fraction. Generally, compared to aluminium, more accurate normalised data can be expected using lithium.

As for clay, no intercept (N_x) applies for organic matter, which is usually represented by **organic carbon**. Organic matter also occurs in the coarse fraction but is even then a co-factor that contributes to the affinity for contaminants, whereas the aluminium in the coarse fraction does not. Furthermore, organic matter in a sample is not always well defined as it can be composed of material with different properties. The most variable properties will be found in the organic matter present in the coarse fraction, i.e. that not associated with the fines. In **fine sediments** or in the sieved fine fractions the majority of the organic matter is associated with the mineral particles and it is assumed to be of more constant composition than in the total sample. In addition, the nature of the organic matter may vary. For samples with low organic carbon content close to the detection limit, normalisation using this co-factor suffers from a large relative error. This results from the detection limit and the insufficient homogeneity that cannot be improved due to the limited intake mass for analysis.

For further interpretation of data, the **proportion of fines** determined by sieving can be useful. Provided there are no significant amounts of organic matter in coarse fractions, the proportion can be used as a normaliser, particularly for organic contaminants. The error in the determination of fines has to be taken into account and will be relatively high for coarse samples.

7. Considerations on contaminants

Almost all trace metals, except mercury and in general also cadmium, are present in the coarse mineral matrix of samples. The metal concentrations show a spatial variability depending on the origin of the sandy material. In sandy sediments, partial digestion techniques result in lower values than are obtained from total digestion techniques. This implies that partial digestion results in lower intercepts (pivot point is closer to the zero). However, the partial digestion must be strong enough so the clay will be totally digested (as is the case with HF digestion techniques), and the measured aluminium content remains representative for the clay. It was demonstrated that analyses of fine material gave similar results for several trace elements using both total and strong partial methods (Smedes *et al.* 2000, Kersten and Smedes, 2002, cf. Technical Annex 6).

In general, correlations of organic contaminants with organic carbon have no significant intercept. Obviously a normalised result from a coarse sample will show a large error as due to the dilution by sand the concentrations are often close or even below the detection limit. Presently, organic carbon is usually applied for normalisation of PAHs. It should be recognised that due to the possible presence of undefined mate-

rial, for example soot or ash, elevated PAH concentrations may occur in specific fractions that might have limited environmental significance. Although this needs further investigation, existing results indicate that PAH concentrations in the sieved fractions are not affected significantly.

8. Isolation of fine fractions for analyses

The Sample preparation

Samples must be sieved at 2 mm as soon as possible after sampling to remove 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. Until the final sieving procedure that isolates the fines, the sample can be stored at 4°C for about a week and up to 3 months 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. Air-drying is not appropriate due to high contamination risks. Besides, samples may be difficult to disaggregate and mineral structures may be affected.

Requirements for Sieving

A wet sieving procedure is required to isolate the fine-grained fractions (<63 µm or <20 µm). Wet sieving re-suspends fine particles that would otherwise remain attached to coarser particles in the sample. Sediments should be agitated during sieving to disaggregate agglomerates of fines and to prevent clogging of the mesh. Freeze-dried samples need to be re-suspended using ultrasonic treatment. Seawater, preferably from the sampling site, should be used for sieving as it reduces the risk of physico-chemical changes in the sample i.e. losses through leaching or contamination. Furthermore seawater assists the settling of fine particles after the sieving. If water from the sampling site is not available, then seawater of an unpolluted site, diluted with deionised water to the required salinity, can be used. The amount of water used for sieving should be kept to a minimum and be reused for sieving subsequent batches.

To minimise or prevent contamination it is recommended to use large sample amounts of sediment for sieving. No significant contaminant losses or contamination was detected when at least 25 g of fine fraction is isolated. (QUASH).

Methodology

Both automated and manual methods are available for sieving. A video presentation of these methods can be provided by the QUASH Project (QUASH 1999).

- The automatic sieving method pumps seawater over a sieve that is clamped on a vibrating table (Klamer *et al.* 1990). The water passing the sieve is lead to a flow-through centrifuge that retains the sieved particles and the effluent of the centrifuge is returned to the sieve by a peristaltic pump. Large sample amounts, up to 500 g, can be handled easily.
- The second method is a manual system sieving small portions 20-60 g using an 8-cm sieve in a glass beaker placed in an ultrasonic bath (Ackermann *et al.* 1983). Particles are isolated from the water passing the sieve by batch wise centrifugation. The water can be reused for a subsequent batch of sediment. In case of sandy samples, when large amounts of sediments have to be sieved, removal of the coarse material by a pre-sieving over e.g. 200-µm mesh can facilitate the sieving process.

Isolated fine fractions have to be homogenised thoroughly, preferably by a ball mill, as centrifugation produces inhomogeneous samples due to differences in settling speed of different grain-size fractions.

9. Limitations of normalisation

The purpose of normalisation is to reduce the variability between samples arising from differences in bulk sediment properties. However, it has been observed in some areas that the correlations between contaminant and co-factor concentrations may be weak or even absent. This may happen, e.g., if the co-factor used is inappropriate for the contaminant of concern, the degree of contamination is very variable with time or space, or there is significant additional variance arising from the measurements of the concentration of the chosen co-factor.

Contracting Parties may specify co-factors other than Al, Li or TOC to be used for the normalisation of concentrations of particular contaminants in their monitoring data. The effectiveness of the normalisation should be assessed through the effect of application of normalisation on the residual variance about time series, as described above. When making proposals, it will be necessary for CPs to ensure that pivot values and Background Concentrations expressed in relation to the same normalisers are also available.

Current procedures applied by OSPAR MON in assessing time series of data include the application of smoothers or, for short time series, linear regressions. Normalisation by co-factors should be applied if this results in a reduction of the residual variance around the fitted smoother or regression in time series, but should not be applied if the residual variance is not reduced. In case the residual variance can be reduced for time series, normalisation should also be applied to check whether observed concentrations of contaminants are at or close to Background (Assessment) Concentrations and whether they comply with the Environmental Assessment Criteria.

Furthermore, as the composition of sand-sized material may differ significantly between different parts of the Convention area, **pivot values** (cf. section 5) can vary, too. In addition they can vary with the analytical method, i.e. with partial or total digestion. The use of inappropriate pivot values could have significant impact on the calculated normalised concentrations (cf. section 5), particularly for sediment samples containing relatively small proportions of fine grained material. Therefore, Contracting Parties may derive pivot values appropriate to particular parts of the Convention area. Such regionalised pivot values should be applicable over large parts of the Convention area, for example across entire Regions, or to all monitoring data from a particular Contracting Party. In the absence of accepted new proposals, the current pivot values (OSPAR 2008) will be used.

The current **Background (Assessment) Concentrations** may be inappropriate for application throughout the Convention area, as they were derived from a data set that emphasises the northern part of the Convention area. In addition, the Background Concentrations are currently expressed as normalised values (to 5% aluminium for metals and 2.5% TOC), and “reference” values of the co-factors may not be appropriate for all areas. The use of inappropriate values for Background Concentrations could result in misleading assessments, e.g., as to whether concentrations in sediment are at or close to background. Therefore, Contracting Parties may derive Background Concentrations and associated co-factor values that they consider to be appropriate to particular parts of the Convention area. The combinations of Background Concentrations and associated co-factor values should be consistent with the way in which

pivot values to be used in the assessment of the field data are expressed, to allow the construction of straight lines joining pivot values and Background Concentrations. Such regionalised Background Concentrations should be applicable over large parts of the Convention area, for example across entire Regions, or to all monitoring data from a particular country. In the absence of accepted new proposals, the current Background Concentrations and cofactors should continue to be used.

10 Upper assessment criteria – EACs, etc

The 2008 OSPAR MON assessment of contaminant concentrations in sediment employed two types of assessment criteria. One of these (termed T_0 in their report) was used to assess whether concentrations were at or close to background, ie the T_0 criteria were the Background Assessment Criteria.

The upper type of assessment criteria (termed T_1 in their report) were used to assess whether the concentrations observed were below levels that were unlikely to result in unacceptable biological effects. The appropriate OSPAR criteria are EACs, but MON found that EACs were not available for all the contaminants of interest. Specifically, EACs for sediment were available for PCBs but not for metals or PAHs. In order to have a complete set of criteria, MON used ERL values for metals and PAHs. MON expressed the concentrations of all contaminants in normalised form for the purpose of trend assessment, and for comparison with BACs, which are expressed as normalised concentrations. For consistency, MON made comparisons between normalised concentrations and EACs/ERLs. While EACs for PCBs are expressed as concentrations normalised to TOC, ERLs are expressed on a non-normalised basis. It has been argued that comparison of normalised field data with non-normalised ERLs is inappropriate.

The preceding text indicates that the MON assessment procedure be amended to allow for an increased level of flexibility in the application of normalisation procedures, pivot values and BCs. It may also be appropriate to revisit the current assessment procedure against EACs/ERLs with a view to introducing a parallel degree of flexibility in the expression and testing of data against these T_1 criteria.

11. Spatial monitoring in the CEMP

Historically, OSPAR has on occasion organised large scale spatial monitoring programmes to describe the spatial distribution of contaminants in the marine environment. However, such programmes have not been undertaken for many years for the more established contaminants.

The 2007 revision of the OSPAR Coordinated Environmental Monitoring Programme describes the role of spatial monitoring in CEMP. There are two primary roles:

- i) “if an area of concern is identified in a spatial programme, a temporal trend programme may be implemented at a limited number of representative sites;”

A purpose of spatial monitoring is therefore to identify areas for more thorough temporal trend monitoring. An example of this could be a proposal for “one-off” surveys of a group of emerging contaminants. A possible survey design would be to measure these contaminants (mainly in sediment) in a series of major river estuaries to detect the important areas of input for potential future monitoring. Such exploratory scoping programmes will usually lack underlying knowledge of the behaviour of the new contaminants

A second purpose for spatial monitoring is:

- ii) if a temporal trend changes unexpectedly, a spatial programme may be used to identify contaminant sources or the extent of the problem."

This is a form of investigative monitoring, by which an unexpected problem or feature of data is identified and a programme is subsequently designed to investigate the cause and scale of the effect.

Both of these purposes are rather specialised, and it is difficult to give reliable guidelines on the need for, or nature of, appropriate normalisation of concentrations of contaminants in sediment. For example, it is unlikely that there will be enough underlying information concerning emerging contaminants to be able to specify the best normalisation methods, and almost by definition there will be insufficient data to establish BACs or EACs.

In the second case, the nature of investigative programmes will be very dependent on the problem being investigated, and details of its geographical location. The objective will be to answer the specific issue that made the investigation necessary. Investigative programmes will need great flexibility and will be specifically designed to address unexpected features in local data. It is therefore difficult to specify how data from such an investigation should be handled.

In both cases, therefore, the group managing the programme must be aware of the potential of differences in bulk sediment properties to influence their data and to take account of this in their data interpretation. However, the variable and unpredictable nature of these surveys and their results mean that rigid definition of approaches to data interpretation would be inappropriate.

12. Recommendations

- 1) For monitoring, it would be ideal to analyse samples with equal composition. This could be confirmed by determination of co-factors Al, Li, OC and parameters of the grain size distribution (e.g. clay content, proportion <20µm, proportion <63µm). However, this situation will not always occur.
- 2) New temporal trend programs should be carried out by the analysis of fine sediments or a fine-grained fraction, isolated by sieving. Existing temporal trend programs could be continued using existing procedures, provided that assessment of the data indicates that the statistical power of the programs is adequate for the overall objectives.
- 3) Contaminant concentrations in whole sediments can be subjected to normalisation using co-factors for organic matter, clay minerals etc., taking into account the presence of both co-factors and target contaminants in the mineral structure of the sand fraction of the sediment. Taking into account these non-zero intercepts of regressions of contaminant concentrations with co-factors, normalisation to preselected co-factor content will reduce the variance arising from different grain sizes. Normalised values for sandy sediments will have greater uncertainties than for muddy sediments. The propagated error of the variables used for normalisation may be unacceptable high for sandy sediments, if both contaminant and co-factor concentrations are low, particularly when approaching detection limits. In that case, in order to reduce the overall uncertainty, alternative procedures, such as sieving, need to be used to minimise the impact of this error structure.

- 4) The natural variance of sample composition will be smaller in the fraction <20 μm than in the fraction <63 μm . Therefore, for trace metals, the fraction <20 μm should be preferred over the fraction <63 μm . However, separation of the fraction <20 μm can be considerably more laborious than the separation of the fraction <63 μm and might be an obstacle to its wide application. For this practical reason, the fraction <63 μm is an acceptable compromise for monitoring programmes. For organic contaminants, the fraction <63 μm should be used for analyses, as it may be difficult to incorporate the organic matter with the highest binding capacity for organic contaminants in the fine grained fraction <20 μm completely. Thus, variances due to separating the fine fraction can be reduced.
- 5) There will still be some residual variance arising from differences in the composition (mineralogy and organic carbon content) of the sediments. Therefore, the preferred approach is analyses of contaminants in fine sediments or in the fraction <63 μm , followed by normalisation of analytical results using co-factors (see section 3). Current scientific knowledge indicates that this procedure minimises the variances arising from differences in grain size, mineralogy and organic matter content. Application of this two-tiered approach to fractions <20 μm gives results that can be directly compared to results found by normalisation of concentrations measured in fractions <63 μm .
- 6) In order to clarify aspects of data interpretation, analytical data for field samples should be accompanied by information on limits of detection and long term precision. In order to contribute to environmental assessment, data for field samples should include the grain size distribution, as a minimum the proportion of the analysed fraction in the original whole sediment. Aluminium (Al) and total organic (TOC) concentrations should be reported for use as potential normalisers. If possible, the determination of Li as an additional potential normaliser is recommended.
- 7) In order to take into consideration potential regional differences in sediment composition in monitoring contaminants in sediments and its assessment, normalisers others than mentioned in section 3 may be used. Furthermore, regionalised pivot points for calculating normalised contaminant concentrations as well as regionalised Background (Assessment) Concentrations may be derived for different regions.
- 8) In order to take into consideration potential regional differences in sediment characteristics and normalisation procedures, it is recommended that the current assessment procedure against EACs/ERLs be revisited with a view to introducing a degree of flexibility in the expression and testing of data against these criteria.
- 9) In the case of spatial monitoring, exploratory scoping programmes will usually lack underlying knowledge of the behaviour of the new contaminants, and of assessment criteria such as BACs or EACs. Investigative programmes will be very dependent on the problem being investigated, and details of its geographical location, and will need great flexibility to be able to effectively address unexpected features in local data. It is therefore difficult to specify how data from either kind of programme should be handled. In both cases, the group managing the programme must be aware of the potential of differences in bulk sediment properties to influence their data and to take account of this in their data interpretation.

However, the variable and unpredictable nature of these surveys and their results mean that rigid approaches to data interpretation would be inappropriate.

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Appendix

Testing normalisation methods

As normalisation should correct for sediment composition, a criterion for an adequate normaliser is that after normalisation of equally polluted sediment samples with different grain size distributions, the results should not differ significantly. However, sample sets to test normalisation approaches for this criterion are scarce. An alternative approach is to take one sample and to produce subsamples with varying grain size distributions (Smedes 1997; Smedes *et al.* 1997; Smedes *et al.*, 2000). Both the fine and coarse subsamples are analysed for contaminants and potential normalisers. In this way a higher variability for the normaliser concentrations, i.e. a worst case than ever will occur in nature, can be obtained which provides a sensitive test for the effectiveness of potential normalisers.

Normalisation is intended to correct for sediment composition for sediments that are equally polluted. Here equally polluted means that the sediments are in equilibrium with the same water. Normalised results should not significantly differ for sediment samples with different grain size distributions

To test which parameters, i.e. co-factors, are suitable for a certain area, a set of equally polluted samples should be collected. In practice this is often problematic as often pollution is not homogeneous in the area and/or the range in grain size that can be collected is too limited to properly demonstrate relations between co-factors and contaminants.

However, this can also be addressed through an active approach which is applicable to all areas (excepting areas where sediment is dominated by only sand or gravel). Smedes *et al.* 1997 used pairs of sieved and unsieved samples to test co-factors. In the EU QUASH project, survey and intercalibration samples were actively separated in different grain size fractions (Smedes *et al.* 2000). To adopt this approach, the following procedure is suggested. A large sediment sample (3 liter or more), containing sand as well as fine material, is taken. This sample is transferred to a glass bottle and liquified using local water and then shaken, tumbled or mixed for at least one month. The sediment is then separated into subsamples with different grain size compositions by sieving and decantation. A range of fractions can be separated, for example <20µm, <63µm, >63µm etc and, of course, also the unfractionated sediment is part of the set.

A decantation procedure will give another type of sample. Suspend the sediment in the local water used for shaking and wait a short time to allow the coarse material to settle. Then quickly pour off (part of) the upper water into a second container. Let the particles settle and pour the water back, with the residual coarse material, and repeat until sufficient fine material has been separated for analysis. It is also possible to sieve only at 20µm and mix the <20µm and the >20µm in different proportions creating a series of equidistant compositions.

It is suggested that the approach described above also includes the estimation of pivot values. Therefore a portion of coarse sediment, i.e. >63µm, is treated with ultrasonic so fine material attached to the coarse is released. This fine material is washed out and if sufficient can be analysed also. The coarse sample is added to the sample set.

Results from such an exercise are given below. Here 10 kg sediment from 6 different positions was equilibrated by tumbling for 3 months in excess water. In this research project, organotin compounds were added to investigate their distribution over grainsize fractions (Smedes and Nummerdor, 2003⁴). In Fig 1-4, the relations of cofactors and some metals are given for several stations. The extreme differences in composition caused by the separation process allow demonstration of the relations over large concentration ranges. Also, some rather extreme samples (like very coarse floating material that was sometimes present in low quantities, typically 0.1–0.5%) were isolated when present. This material had a very high organic carbon content, very low mineral cofactors and a higher OC/N ratio than the rest of the fractions. In Fig. 4, this sample is the outlier (open symbols) in the relations. Basically these fractions have no meaning as they are of very low abundance but they give some indication of whether target elements or compounds show a preference for organic carbon, although it should be considered it is not the typical OC as is normally found from humic and fulvic residues.

Values close to the origin also allow derivation of pivot values, although this was not the focus of the QUASH project. Figure 5 shows cofactor and zinc data for all stations in the fraction >63µm; only a few of these were ultrasonically treated. For the Dutch coastal area, the pivot value for Zn can be estimated at about 14–15 mg/kg and for Al and Li at around 4 g/kg and 4 mg/kg respectively.

Application of this process will provide robust information and allow optimization of normalisation for a certain location and will show what bias or variability may be expected from the use of non-regionalised values for pivot points in the procedure for normalisation.

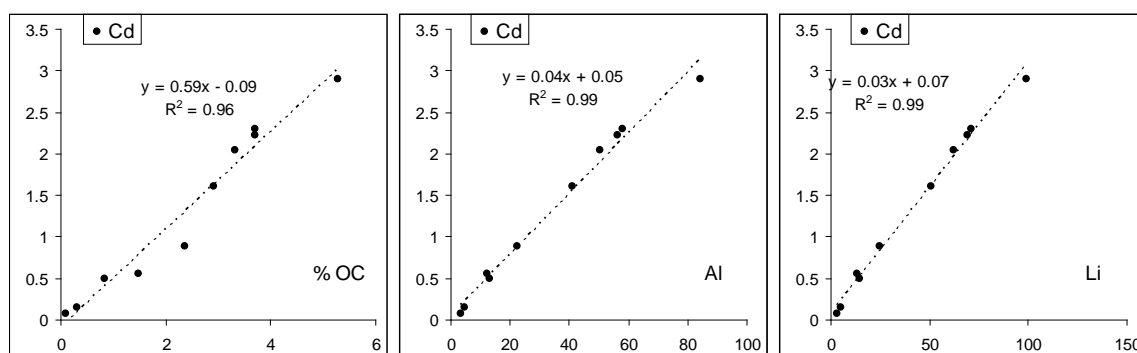


Figure 1. Cd and cofactors in Rotterdam harbour area.

⁴ Smedes, F., and Grietje, A., and Nummerdor, N. 2003. Grain-size correction for the contents of butyl compounds in sediment. RIKZ\2003.035. ISBN 03693477x, National Institute of Coastal and Marine Management (Rijksinstituut voor Kust en Zee), RIKZ, PO Box 20907, 2500 EX, The Hague, The Netherlands.

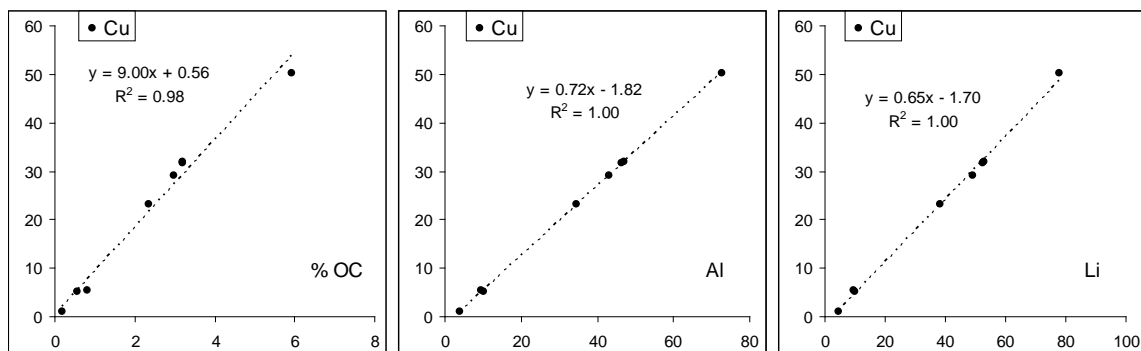


Figure 2. Cu and cofactors in Nieuwe Waterweg towards Sea.

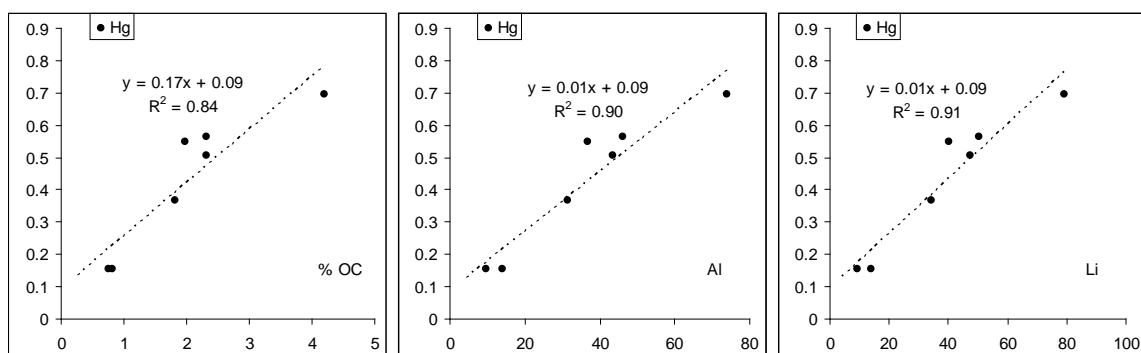


Figure 3. Hg and cofactors in sludge dump site at Sea.

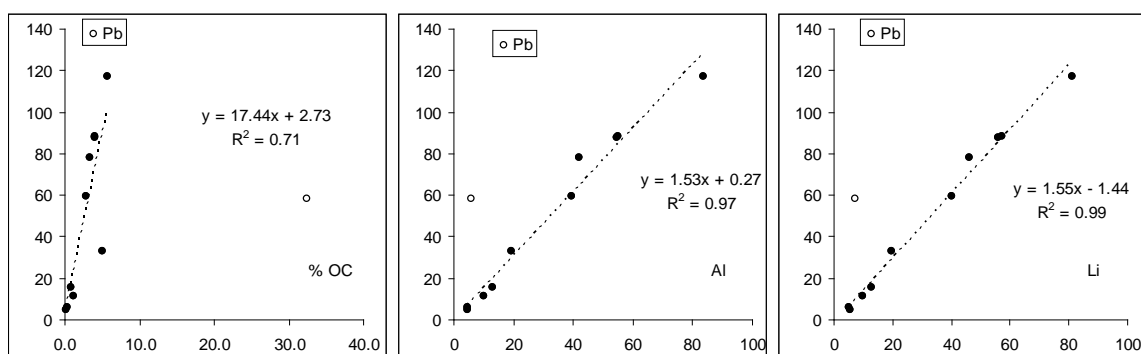


Figure 4. Pb and cofactors in front of IJmuiden Harbor. Note that one outlier is omitted. This is from coarse floating material with high OC content and representing less than 0.2% of the sample weight.

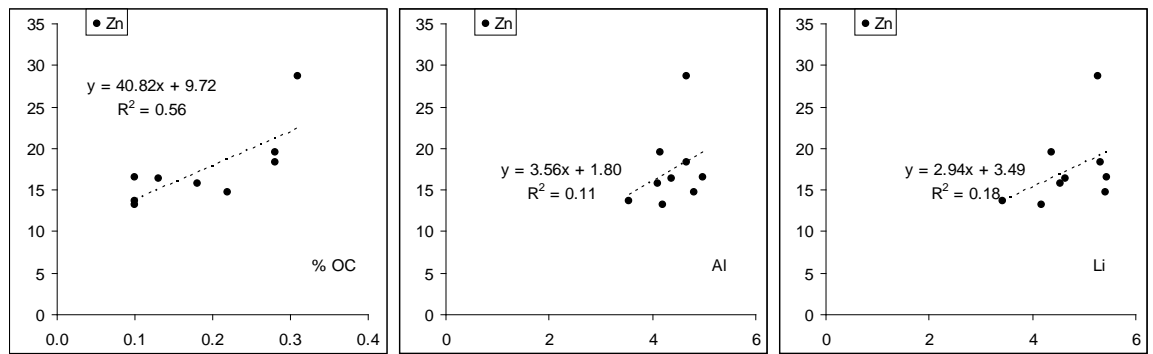


Figure 5. Zn and cofactors in only the >63 samples.

Annex 6: Action list

AGENDA ITEM	ACTIONN	Who
c	To report on the uncertainty in data assessments arising from the selection of co-factors.	Claire Mason and Stefan Schmolke
e	Continue collection of data and develop background concentrations for alkylated PAHs.	Lucia Viñas (lead)
e	Send BC data on alkylated PAHs to Lucia	All members
g	A review of partition coefficients for organic contaminants in sediments.	Stefan Schmolke
h	Finalise the technical annex to the JAMP Guidelines for monitoring of dioxins in sediments.	Patrick Roose (lead)
-	Evaluate the continuation of the work on ratios	Stefan Schmolke, Foppe Smedes and Ian Davies

Annex 7: Recommendations

RECOMMENDATION	FOR FOLLOW UP BY:
1. MON should consider the suggestions made by WGMS in future assessments of contaminant concentrations in sediments.	OSPAR MON
2. WGMS recommend that work on sediment dynamics is to be continued, paying special attention to areas that have not been dealt with. Publication of dynamics research report should be considered as the first of an intended series.	WGMS, SCICOM
3. Continue the ICES input, e.g. through the WGMS chair, in the process on the development of a Guidance document on Chemical Monitoring of Sediment and Biota under the Water Framework Directive. Ultimately, the WFD Guidelines should resemble the OSPAR Guidelines as closely as possible, particularly in the case of the normalization technical annex reviewed and updated during this meeting. This will be increasingly important in the implementation of the Marine Strategy Framework Directive.	Chair WGMS, SCICOM, ACOM
4. WGMS recommends that attempts to derive background concentrations should be forwarded to OSPAR.	ACOM, OSPAR
5. WGMS recommends that the updated Technical Annex on Normalisation be forwarded to OSPAR	ACOM, OSPAR
6. WGMS noted that the sediment guideline itself is outdated and recommends that OSPAR considers revising it.	ACOM, OSPAR
7. WGMS recommends that the ICES Data Centre use the information on station in the station dictionary to complete the depth field.	ICES Data Centre

Annex 8: WGMS terms of reference for WGMS 2010

2009/2/SCICOM00 The **Working Group on Marine Sediments in Relation to Pollution** [WGMS] (Co-Chairs: Patrick Roose, Belgium, and Lucía Viñas) will meet from [to be decided 2010] in San Sebastian, Spain, to:

Sediments monitoring

- a) Review and comment on the report of the 2009 meeting of OSPAR/MON in relation to sediments.
- b) Review information relevant to the regionalisation of pivot values and background concentrations of contaminants in sediment.
- c) To report on the uncertainty in data assessments arising from the selection of co-factors.

Sediment dynamics

- d) To develop plans for a further cooperative research report on the implications of sediment dynamics for the organisation and interpretation of sediment monitoring.

Background concentrations

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

Passive Sampling

- f) Report ongoing and new projects involving passive sampling:
 - Projects that combine biological effects measurements with passive sampling;
 - National projects involving the use of passive samplers;
 - International cooperative projects involving passive sampling, including the ICON project;
- g) Undertake a review of partition coefficients for organic contaminants in sediments.

Developments of monitoring guidelines

- h) Finalise the technical annex to the JAMP Guidelines for monitoring of dioxins in sediments.
- i) Finalise the technical annex to the JAMP Guidelines for monitoring of monitoring of PFOS in sediments.
- j) Finalise the technical annex to the JAMP Guidelines for monitoring of chlorinated biphenyls in sediment.

Miscellaneous

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

WGMS will report by [DATE] for the attention of the Science Committee (SCICOM).

Supporting Information

Priority:	This Group handles key issues regarding monitoring and assessment of contaminants in sediments.
Scientific justification and relation to action plan:	<ul style="list-style-type: none"> a) Anticipating that the report of the proposed 2009 assessment will be available before the meeting, WGMS can review and comment the progress made; b) Background values and pivot values play an important role in the OSPAR assessments of contaminants in sediments. The regional character of both has thus far not been considered fully. WGMS will review any relevant information for regionalisation of both and advise accordingly. c) The uncertainty associated with the use of co-factors has potentially a significant impact on data assessments. WGMS will investigate this and advise accordingly. d) The sediment dynamics paper has not covered all possible scenarios. WGMS will investigate additional scenarios and the impact of sediment dynamics on the interpretation of monitoring data. e) WGMS has proposed background concentrations on available information. However, the amount of available data is sparse. Additional information may warrant revision of the proposed background concentrations (OSPAR request 3, 2007) f) The combination of passive sampling with biological effect measurements is a strong approach to the coupling of a measure of contaminant exposure and biological effect. It is directly relevant to integrated approaches to monitoring (c.f. WKIMON) and to international initiatives on environmental health assessment (e.g. ICON project). Receiving and review of national reports of projects involving the use of passive samplers by WGMS will build further experience on the field and use of passive sampling. Review by WGMS will contribute to the ICON objectives. g) Partition coefficients play an important role in h) This is the follow up of an OSPAR request (OSPAR request 4, 2008). i) This is the follow up of an OSPAR request (OSPAR request 4, 2008). j) This is the follow up of an OSPAR request (OSPAR request 4, 2008). k) Response to internal ICES requests.
Resource requirements:	None required
Participants:	The Group is normally attended by some 20 members and guests.
Secretariat facilities:	None.
Financial:	No financial implications.
Linkages to advisory committees:	ACOM
Linkages to other committees or groups:	WGBEC, MCWG

Linkages to other OSPAR, HELCOM
organizations:

Annex 9: Technical minutes of the JAMP Review Group related to the WGMS 2009 Report

Review group: Jarle Klungsøyr (Chair), Lars Edler, Jose Fumega, Carlos Vale, Ian Davies, Francis O'Beirn

Expert Group's involved: WGMS, MCWG, WGHABD, BEWG, SGIMC

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

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

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

Comments by RG

In response to OSPAR work requests to ICES to to prepare *technical annexes* for analysis of certain groups of organic contaminants for inclusion in the *JAMP guidelines for monitoring contaminants in marine biota and sediments* MCWG2009 delivered several products to support coordinated monitoring activities.

MCWG 2009, Annex 7 – Planar CBs in biota

An updated version on the analysis of planar CBs in biota has been finished and is put into the Revised Organic Contaminants in biota Technical Annex. MCWG suggests that the existing OSPAR guidelines for monitoring contaminants in biota could benefit from some restructuring. The technical annex on organic contaminants in biota could preferably be split into a part that deals with sampling and sample handling common to all types of organic contaminant analysis under JAMP, and the analysis of CBs could become a separate technical annexes linked to the first. Other organic contaminant groups could then be added as separate annexes. The RG basically support that this is a good suggestion.

The technical annex on “Determination of chlorobiphenyls in biota – analytical method” answers the request from OSPAR for an updated guideline including also planar CBs. The text covers relevant topics and is fit for purpose. If considered for publication it suggested that the text should go through technical editing. This is a general remark to all the prepared technical annexes of MCWG 2009.

MCWG 2009, Annex 8 – Planar CBs in sediments

Analysis of planar CBs has now been included in “Revised technical annex on analysis of PCBs in sediments”. The quality of the revised text is appropriate and should be fit for purpose.

MCWG 2009, Annex 9 – Dioxins/furans in marine biota.

One separate annex has been prepared “Technical Annex on dioxins/furans and dioxin-like PCBs in biota”. The quality of the revised text is appropriate and should be fit for purpose.

MCWG 2009, Annex 10 – Perfluorinated compounds (PFCs) in sediments.

The content of the technical annex on PFCs, including methods for analysis of PFOS and a number of other perfluorinated compounds in sediment, is appropriate and should be fit for purpose.

MCWG 2009, Annex 11 – Perfluorinated compounds (PFCs) in seawater.

The technical annex on PFCs in seawater is appropriate and should be fit for purpose. The technical annex is partly based on the new ISO25101 guideline but is adapted for water samples containing suspended particle matter (SPM) and broadened to cover the analysis of other PFCs besides perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA).

Annex on analyses of dioxines/furans in marine sediments has not been prepared but will be completed 2010 as a joint effort for MCWG and WGMS. At the WGMS 2009 a first draft was prepared which provides some advice on the main steps of the analytical procedure to determine PCDDs and PCDFs in marine sediments. It is mainly based on EPA Method 1613 B (US EPA, Method 1613 Revision B, 1994) that seems to be the most generally accepted method by laboratories involved with dioxin analysis. This document will be completed intersessionally.

MCWG 2009 developed a document on background concentrations for dioxins in marine biota. The approach first taken for developing background concentrations for contaminants in biota was to consider a percentile of contaminant data from areas that could be considered “remote” or “pristine” as a basis for recommending *low concentrations*. However, very few data were available in remote locations for the preferred species/matrix combinations. Most of the information available was from sampling in coastal areas, and data from coastal areas were therefore used. The medians of minimum values as indicative of low concentrations suggested were: 0.15 pg WHO-TEQ PCDD/F g⁻¹ wet weight for marine fish muscle, and 0.06 pg WHO-TEQ PCDD/F g⁻¹ wet weight for bivalve molluscs. It was realized that these are crude estimates based on very limited data. MCWG 2009 did not foresee any substantial additional information being available in the near future. RW took note of this conclusion and support this information be sent to OSPAR.

WGMS 2009 concluded that the data collected so far for dioxines/furans in marine sediments were not sufficient to allow a reliable expression of background conditions and recommends that work be undertaken to collect other data and their appropriate cofactors. RG took note of this conclusion and recommends this message be forwarded to OSPAR.

8/2009. Update of JAMP guidance on normalisation of contaminant concentrations in sediment

To update the technical annex on normalization of contaminant concentrations in sediments contained in the JAMP Guidelines for monitoring of contaminants in sediments. The update should ensure that the technical annex is fully applicable across the OSPAR maritime area.

Comments RG:

WGMS 2009 has handled and updated the Technical Annex 5 on normalisation. The annex is largely complete for normalisation for comparisons with BC/BAC assessment criteria. The task is less complete for the EACs, many of which are not available. Resort to using US EPA ERL values should be seen as an interim measure until reliable EACs can be developed. This has been discussed in the WGMS 2009 report and also in the technical annex (section 10). The text to a large extent refers to details of a MON discussion, and it can be questioned how appropriate this is for a guideline document. RG therefore suggest this text be deleted from the technical annex on normalisation (section 10). The text can be presented in WGMS 2009 report as useful background information. The technical annex on normalisation in its present form allows for a sufficient degree of flexibility in how and when normalisation should be applied. RG supports that the technical annex can be forwarded to OSPAR.