

**REPORT OF THE
WORKING GROUP ON MARINE SEDIMENTS
IN RELATION TO POLLUTION**

**Instituto Hidrografico, Lisboa
5–9 March 2001**

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1 OPENING OF THE MEETING

The Acting Chair, Dr S.Rowlatt, opened the meeting of the Working Group on Marine Sediments in Relation to Pollution (WGMS) at 10.00 hrs on 5 March 2001 at the Instituto Hidrografico, Lisboa. Technical Director Augusto Ezequiel gave a speech of welcome. Dr Rowlatt thanked Mr Ezequiel and outlined the programme for the week.

2 ADOPTION OF THE AGENDA

No formal agenda had been set, rather the Terms of Reference, set for the group by the parent committee, were taken as a working agenda (Annexes 1 and 2). It was decided to intersperse “terms of reference” items with talks by members of the WGMS on their research projects. The list of participants is attached as Annex 3.

3 ARRANGEMENT FOR THE PREPARATION OF THE REPORT

The Chair agreed to prepare the report in collaboration with all the participants. Individual members agreed to prepare particular parts of the report on topics of interest.

4 TERMS OF REFERENCE FOR FUTURE MEETINGS OF WGMS

During the whole week, the issue of a new Chair for WGMS was discussed, both inside and outside the meeting. The Chair is normally appointed for a period of three years, but the Group may alter this duration under special circumstances. The proposed Chair needs to be accepted by the parent committee (MHC) and his/her Delegate to ICES. Some way through the week, and after protracted discussions on a possible new Chair and on the method for electing such a person, an election was held. At this time, Foppe Smedes was unanimously nominated for consideration by the Marine Habitat Committee as a potential new WGMS Chair.

Possible areas of work for the WGMS that had been highlighted in recent meetings were: sediment processes; integration of sediment data and biological effects; interpretation of contaminant data so that it is meaningful to end users (e.g., assessment criteria, environmental indicators and standards). The work suggested could be both relevant to ICES Member Countries and scientifically interesting:

- Processes, such as degradation of organic contaminants, sediment-water interaction and related fluxes, speciation of metals, early diagenesis, bioturbation and their significance to the potential risk to biota.
- Dynamics of the environment, such as permanent sedimentation, highly dynamic environments, bioturbation, and interaction of contaminants between water and sediments, and transport over larger areas.
- Sediment quality criteria, and the establishment of approaches to reach such criteria.
- Methodology related to spatial and temporal monitoring of sediment quality.

The group feels it needs additional expertise in the fields of ecotoxicology and recommends a joint meeting with WGBEC, probably in 2002.

WGMS stated that it welcomes comments on these terms of reference, and explicitly invites its members that could not be present to express their views, and comment, add or clarify the above statements.

5 SEDIMENT STANDARDS

WGMS discussed the definition of sediment standards. It decided to produce an Annex (Annex 4) to this report describing some of the difficulties associated with using various methods for the definition of standards. The group used the work of Peter Chapman as a basis for this Annex.

WGMS felt that a meeting with the Working Group on Biological Effects of Contaminants (WGBEC) should be held in order to move the standards issue forward. The group felt that a joint meeting with WGBEC in 2002 would be appropriate.

6 GUIDELINES

WGMS discussed the requirement to review the Sediment Guidelines, particularly after the comments of ACME 2000 and keeping the needs of the OSPAR Coordinated Environmental Monitoring Programme (CEMP) in mind. The WG therefore gave consideration to Guidelines for both temporal trend and spatial surveys. The interim WGMS guidelines are attached as Annex 5 and a basis for temporal guidelines as Annex 6.

7 PAPER ON NORMALISATION

Michael Kersten had prepared a paper on normalisation. Unfortunately the group did not have time to give this paper the consideration it deserved. It will be discussed intersessionally.

8 NORMALISATION

In 2000, WGMS had a renewed thorough discussion on the need and the effectiveness of different normalisation approaches presented in its report and produced an annex to its 2000 report condensing the outcome of this discussion. As advised by ACME 2000, WGMS 2001 prepared a "Technical Annex: Normalisation of contaminant concentrations in sediments" (Annex 5) based on the 2000 WGMS report. Furthermore, the comments of ACME presented in the 2000 ACME report (Section 6.5), as well as earlier ACME advice, were taken into consideration. In addition, the preliminary outcome of the work package on sieving and normalisation of sediment of the EU-QUASH (Quality Assurance in Sampling and Sample Handling) intercomparison exercise has been taken into account. The Technical Annex on Normalisation annexed to this report as Annex 5 is intended to supplement the Sediment Monitoring Guidelines. It replaces the previous Draft Technical Annex on Normalisation produced in 1998 that had been annexed to the 2000 WGMS report as Annex 4. WGMS intends to include appendices on error calculation and on examples for demonstrating the application of the normalisation approaches presented in the current Draft Technical Annex on Normalisation (Annex 5). However, during the 2001 meeting there was not enough time to complete these appendices and WGMS decided to complete them intersessionally, provided that ACME adopts the current Draft Technical Annex.

Annex 5 gives recommendations for a proper application of different approaches to normalisation and includes their advantages and disadvantages. The preferred approach (recommendation 6 of Annex 5) consists of two steps: analysing contaminants in a fine sediment sample or a sieved fine fraction in order to reduce the analytical uncertainties significantly, followed by normalisation with a co-factor that reduces variances due to the natural variability of the geochemical composition of the samples.

As pointed out in the 2000 ACME report, the widely applied approach of normalising contaminant concentrations that were analysed in the whole sample, i.e., in the fraction <2 mm, with a co-factor, suffers from large uncertainties for samples with high proportions of sand and low concentrations of contaminants and normalisers. WGMS 2001 felt that this drawback is overcome with the recommendation to use fine samples or sieved fine fractions for analyses.

Although ACME 2000 recognised that normalisation of whole samples suffers from large uncertainties with regard to sandy samples, it expressed its concern that a normalisation approach based on sieved sediment might be misleading for some dynamic coastal areas of the Atlantic coast of Europe. However, after discussion, WGMS 2001 concluded that this approach is of great importance particularly for these areas, where normalisation of total samples that often are sandy would result in values with large uncertainties, thus weakening the statistical power of detecting differences in contaminant concentrations.

The preliminary results of the QUASH intercomparison exercises (cf. WGMS 2000, §5) clearly demonstrated that variances could be reduced to a large extent by analysing fine samples or sieved fine fractions and that variances could be further reduced by subsequent normalisation with co-factors.

As the two-tiered approach based on fines had not yet been applied to large areas, such as the OSPAR area, and its reliability had not yet been proved, ACME 2000 recommended for the meantime to avoid wide-scale spatial surveys using fine sediments. WGMS agrees with ACME that this normalisation approach will still not correct for all potential differences in sediment properties. However, after discussion WGMS 2001 came to the conclusion that the normalisation approach based on fines will improve the statistical power to identify temporal trends and spatial differences in contaminant concentrations compared favourably to the normalisation approach based on whole samples. It was pointed out that the normalised data are not meant to and are not appropriate to evaluate contaminant loads existing in a certain area. To avoid any misleading interpretation of data, WGMS followed the ACME recommendation to include a mapping of relevant co-factors in any assessment of spatial data. So far, no better approach for assessing spatial surveys on a large scale than the one based on fines is available. WGMS 2001 therefore strongly recommends the application of the two-tiered approach based on fines. According to the proposed Draft Technical Annex on

Normalisation (Annex 5), data produced with other approaches will not be excluded from the assessment of spatial surveys, however, WGMS strongly recommends that data assessments include the procedural uncertainties.

ACME 2000 considered an increasing complexity of normalisation methods as an obstacle to their application. WGMS 2001 came to the conclusion that a more complex normalisation approach is required, especially if analyses are carried out in whole samples, as a proper regression has to take into account the selected normaliser in the sand fraction as well as the concentration of contaminants. A simple ratio of contaminant/normaliser often can result in misleading data, especially if the data assessment includes sandy samples. When analysing fine samples or sieved fine fractions, normalisation of the measured concentrations with a co-factor is much simpler, as intercepts of the theoretical regression line are small and can therefore be neglected, i.e., a ratio of contaminant/normaliser can be used as a good approach. WGMS 2001 would like to stress that all results used for monitoring have to be accompanied by the procedural uncertainties, in order to facilitate a proper data evaluation. This would result in some additional effort being required.

Furthermore, the 2000 ACME report expressed concern about whether contaminant concentrations measured in a sieved fine fraction may give useful information in relation to biological effects. WGMS recognises this comment and pointed out that normalisation was primarily developed for correction of differences in the composition of sediments. It was stressed that OSPAR Guidelines for Contaminant-specific Biological Effects Monitoring have been developed. Nevertheless, WGMS 2001 considers data derived from sieved fine fractions to be valuable to support the assessment of biological effects as illustrated by the following example: A water-sediment system of 1 litre water and 1 kg very fine sediment has a specified toxicity. Toxicity will not be affected when a stone is added to the mixture. Neither will toxicity be influenced when instead of one big stone several smaller stones nor when a billion inert sand particles are added. Addition of sand will result in a tremendous change of the “analytical concentrations” but not of the toxicity of the system. Normalisation by analysing sieved fractions just aims at correcting for the added inert material in order to exclude its influence on concentrations.

In order to demonstrate the suitability of the preferred two-tiered normalisation approach and to clear up existing doubts, WGMS 2001 suggests initiation of an intersessional study group that will apply all normalisation approaches included in the Technical Annex on Normalisation (Annex 5) to actual data sets. The majority of the work could be carried out by correspondence. The group should consist of members of the WGMS and representatives of monitoring programmes. It would be desirable if the study group could have the support of a statistician.

9 PRESENTATION BY DR CATO

Dr Cato presented a recently published Swedish report (Cato, I., 2000: Toxic substances and environmental quality of the Bohus Coast 1990–1998 — trends, load and relationships. *Geological Survey of Sweden, SGU Rapport och meddelanden 103, 135 p.* Uppsala, ISBN 91–7158–641–5) dealing with the current load and trend of contaminants in sediments and biota during the 1990s along the Swedish West Coast bordering the Skagerrak. The book, which was written on behalf of the Bohus Coast Water Conservation Association, showed a number of interesting results. Sediment and biological samples used in the study were collected five years apart at static sites. The biota investigated were blue mussel (*Mytilus edulis*), bladderwrack (*Fucus vesiculosus*), eelpout (*Zoarces viviparus*) and cod (*Gadus morhua*); at one station crab (*Cancer pagurus*) and green crab (*Carcinus maenas*) were also evaluated. The different media were analysed for 11 metals, DBT, TBT, extractable organically halogenated compounds, 16 PAHs, 7 PCBs, DDTs, HCB, 7 chlorinated aromatics, 10 halogenated aliphatics, 6 monocyclic aromatics, 5 bicyclic aromatics, 6 phthalates, 12 chlorinated and 5 unchlorinated phenols, non-*ortho* PCBs, toxaphene and dioxins/dibenzofurans. The evaluations were conducted to record changes over time, existing concentration relationships between various investigated media and environmental quality according to the Swedish criteria for coast and sea.

The results show that a number of elements and compounds are dispersed along the Swedish Bohus Coast, but that the concentrations of the different elements and compounds vary between different media and sites. The environmental quality (EQ) along the coast varied from sites with good conditions to sites with very bad conditions. The figures showed an excess of harmful substances in the Gothenburg region for all media categories studied. The relationship between the concentrations of the compounds in two different media was tested. Of the 174 selected tests, relationships with $P > 95\%$ were found in one quarter of the cases.

The trend analyses showed that the major trends were concordant between different media and generally show decreasing average concentrations with greater than 90 % probability in about 50 % of the cases between the two investigation phases. In summary, the conditions regarding environmentally harmful substances in both sediment and biota, with a few exceptions, improved along the Bohus Coast during the 1990s.

Dr Cato presented a new searchable Internet meta-database concerning seafloor sediment samples held at European institutions. The database (EU-SEASED) was built up by people from the Geological Surveys of 14 European countries and the work was supported by the European Union MAST III programme. The aim of the project was to provide the means by which scientists, engineers and parties interested in the sea floor can quickly find out what seabed samples have been recovered and where they are stored, thereby promoting secondary usage of this data resource. This optimising of data use will, among others, save a lot of money for society. The web address is <http://www.eu-seased.net>.

The EU-SEASED database will only list metadata, access to samples and access to any related accessory data sets will be for negotiation between the requestor and the repository where the sample is stored. Today the database holds metadata of more than 250,000 sample/coring sites within European waters or deep-sea sites held by European organisations. More than 60,000 visitors per month have been registered during the past months. It is free for all organisations to contribute with more metadata to the database. The database will be kept alive by the MARIS organisation in The Netherlands.

10 RECENT WORK IN THE NETHERLANDS

Hanneke Gieske presented results of two projects: a geochemical baseline study of a part of The Netherlands continental flat (NCP) and a study on the preservation of (contaminated) mud in seabed sediments of the NCP under different dynamic conditions.

The geochemical mapping study dealt with an area north of The Netherlands, between 4°E and 6°30'E and 53°N and 54°N. The aim of the study was to obtain an insight into the spatial distribution of major and minor elements in seabed sediments and to relate the geochemical characteristics of the sediments to the geological and dynamic setting of the area and to anthropogenic inputs. 160 seabed samples and 60 samples from 4 cores with a maximum length of 5 m were analysed with XRF. At depths between 20 m and 40 m highly dynamic sandy sediments occur, with mud contents below 4 % and organic carbon contents below 0.02 %. Deeper than 40 m, in the so-called Oyster Grounds, a slow sedimentation of muddy sediments occurs (estimated rate: 0.2–0.4 cm/yr). Mud contents are between 10 % and 5 %, organic carbon between 0.1 % and 0.6 %.

As expected, concentrations of all elements except SiO₂ are relatively high in the muddy area. From the core samples, regression lines between the heavy metals and Al₂O₃ were calculated, to obtain background values. These calculations showed that Pb was enriched up to 2 times the background mainly in the Oyster Grounds. Zn was less enriched in this area, but in the sandy sediments in the eastern part of the area Zn was up to three times the natural background. This points to an input of Zn from the Ems/Dollard into the area. Also for Cu enrichment up to 2 times the background concentrations occur in the eastern part of the area. Arsenic was slightly enriched in an area where gravely sands covering a Saalian till are exposed at the seabed. This enrichment is thought to be due to natural processes. Ni showed background values in the entire area.

The second study investigated an hypothesis formulated by Laane *et al.* (1998). They reported decreasing concentrations of heavy metals and most organic contaminants in Dutch coastal sediments between 1981 and 1996. They assume that the main reasons for this decline are: (1) the decrease in input from various sources, (2) sedimentation and mixing of less-polluted suspended matter into the active sediment layer, and (3) the washing out of older, more contaminated particles.

In order to investigate which processes can explain the assumed dilution or replacement of “older” mud in the seabed sediments, and to which depth these operate, a combined geochemical and sedimentological approach was applied.

In the dynamic coastal zone and the sand wave field between The Netherlands and the UK, (storm) waves, tides and the migration of bedforms (e.g., sand waves and megaripples) are continuously reworking the seabed sediments in the coastal zone. No permanent sedimentation or erosion takes place here. North of The Netherlands a deeper area (> 40 m) occurs, the Oyster Grounds, where (very) fine sand and silts are deposited. Reworking by burrowing organisms takes place in all areas.

At 14 locations in the coastal zone, the sand wave field and the Oyster Grounds, cores with a length of approximately 5 m were taken. On the basis of their sedimentological characteristics, different “events”, i.e., sediment sequences formed by one event (e.g., a storm), could be distinguished in the uppermost parts of the cores. 180 samples were taken from the cores, well distributed over the different sedimentological events, and analysed for major and minor elements and Pb isotopes by XRF and ICP-MS. From the data set, Pb, Zn and the ²⁰⁶Pb/²⁰⁷Pb-ratio were selected for investigation of the presence of anthropogenically enriched mud. It appeared that in the dynamic coastal zone and sand wave field the active layer (the upper sedimentological events) showed rather constant Pb/Al₂O₃ and Zn/Al₂O₃ values and ²⁰⁶Pb/²⁰⁷Pb-

ratios. Underneath the active layer $\text{Pb}/\text{Al}_2\text{O}_3$, $\text{Zn}/\text{Al}_2\text{O}_3$ and $^{206}\text{Pb}/^{207}\text{Pb}$ -ratios showed background values in most cores. The depth of the active layer was on average 15 cm to 30 cm. In the cores of the muddy Oyster Grounds, the vertical profiles showed a slow decline of concentrations to background at 40 cm to 50 cm depth.

The constant $\text{Pb}/\text{Al}_2\text{O}_3$, $\text{Zn}/\text{Al}_2\text{O}_3$ values and $^{206}\text{Pb}/^{207}\text{Pb}$ -ratios in the active layer in the coastal zone and sand wave field indicate that the time scale on which the sediment is reworked by (storm) waves, tides and migrating bedforms is much faster (days to months) than the time scale on which the contaminant load of the mud declines (years). The active sediment layer therefore probably records the recent contaminant load of the suspended matter in the overlying water column.

In the deeper and quieter environment of the Oyster Grounds, the vertical profile is disturbed ("smoothed") by bioturbation, and the recent decline in heavy metal concentrations cannot be recognised in these sediments.

References

- Gieske, J. M. J., B. J. H. van Os and C. Laban, (in prep). Geochemical baseline mapping of North Sea sediments of the Terschelling Bank area.
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- Laane, R.W.P.M., H.L.A. Sonneveldt, A.J. Van der Weyden, J.P.G. Loch and G. Groeneveld, 1999. Trends in the spatial and temporal distribution of metals (Cd, Cu, Zn and Pb) and organic compounds (PCBs and PAHs) in Dutch coastal zone sediments from 1981 to 1996: a model case study for Cd and PCBs. *Neth. J. of Sea Res.* 41, p 1–17.

11 CONTAMINATED SEDIMENTS IN NORWAY

Dr Naes informed WGMS on actions to be taken in Norway against contaminated sediments. In the coming years efforts on remedial actions in Norwegian fjords and harbours will be under planning. This will require a substantial amount of money actualising the need for a sound scientific basis of the initiatives. To perform the remedial actions in a cost-effective way, site-specific mass balances and food chain accumulation data are needed. Dr Naes informed WGMS of a research project he is heading related to the distribution and effects of dioxins in one of the fjords in Southern Norway. This is a recently started, four-year, multi-institutional research project using a multi-compartmental mass balance model of the fate of dioxins in the fjord environment. The project includes characterisation of selected food webs and the accumulation and effects of dioxins in them as well as development of risk assessment models. Information on the results will be given to WGMS on later occasions.

12 PRESENTATION BY DR BELZUNCE

Dr Belzunce presented an overview of the state of the contamination in the estuaries along the Basque Coast. The results presented are part of a surveillance programme carried out along the Basque Coast since 1994. In this programme, 50 sampling sites have been defined for surface sediments, column water, biota and benthos investigations. In the estuaries, the sediment sampling covers the entire surface of the estuary from the inner to the outer part.

Results on heavy metal concentrations in sediments of six estuaries, Barbadún, Nervión, Butroi, Oka, Lea, and Artibai, with a total of 68 sediment samples, were presented. The heavy metal concentrations show a great variability in their distribution in the estuaries and high concentrations of cadmium, lead and mercury that are above the upper action level defined by the Spanish legislation were found. On the basis of the Pollution Load Index, the Nervión estuary is the most contaminated in the Basque Coast.

The sediments in the estuaries were classified in three categories according to the Spanish Recommendations for sediment management. Most of the sediments from the Nervión estuary are classified into category 2, which implies no disposal of material into the sea without previous control of that material.

13 CLOSURE OF THE MEETING

WGMS agreed on terms of reference for a meeting in 2001, as contained in Annex 9.

The meeting finished at 1500 h on the 9 March 2001. The Chair thanked all members for their hard work as a group and their contribution to the production of the report.

ANNEX 1: AGENDA

- 1) Review and revise Technical Annex 2 of the Sediment Guidelines on Normalization taking into account the comments by ACME.
- 2) Review existing information for estimating and validating contaminant fluxes and budgets for sediment-water systems, especially with respect to recent information on the equilibrium partitioning of pollutants between sediment and water.
- 3) Consider a report on processes, such as speciation of metals and their diagenetic interaction, in relation to contaminants in sediments.
- 4) Consider information on the dynamics of the environment, such as permanent sedimentation, highly dynamic environments, bioturbation, interactions of contaminants between water and sediment and over larger areas, and their significance to biological effects.
- 5) Review the methods to define sediment quality criteria, taking account of experience in The Netherlands, USA, Canada, and Australia (in order to initiate cooperation between WGMS and WGBEC, the Chairs will communicate intersessionally, and the review will be made available to WGBEC before their meeting).
- 6) Recommend a methodology that provides the basis for spatial and temporal monitoring of sediment quality, particularly taking statistical aspects into consideration (this should include intersessional discussions with statisticians).

ANNEX 2: TERMS OF REFERENCE

The **Working Group on Marine Sediments in Relation to Pollution** [WGMS] (Chair: Dr S. Rowlett, UK) will meet in Lisbon, Portugal from 5 to 9 March 2001 to:

- a) finalise Technical Annex 2 to the sediment guidelines (Normalisation);
- b) consider a report on processes, such as speciation of metals and their diagenetic interaction, in relation to contaminants in sediments;
- c) consider information on the dynamics of the environment, such as permanent sedimentation, highly dynamic environments, bioturbation, interactions of contaminants between water and sediment and over larger areas, and their significance to biological effects;
- d) review the methods to define sediment quality criteria, taking account of experience in The Netherlands, USA, Canada, and Australia (in order to initiate cooperation between WGMS and WGBEC, the Chairs will communicate intersessionally, and the review will be made available to WGBEC before their meeting);
- e) recommend a methodology that provides the basis for spatial and temporal monitoring of sediment quality, particularly taking statistical aspects into consideration (this should include intersessional discussions with statisticians).

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ANNEX 4: REVIEW OF SOME METHODS USED FOR SETTING SEDIMENT QUALITY GUIDELINES

DRAFT

Several different approaches have been used for setting sediment quality guidelines (SQGs). These are listed in this section together with the advantages and disadvantages of each method. Ingersoll *et al.* (1997) give helpful criteria for evaluating SQGs. As a minimum, reliable and useful SQGs should provide tools that are predictive of the presence of toxicity or other effects, and which demonstrate a dose-response relationship to chemical concentrations calibrated to the SQGs.

1 Background sediment chemistry

The background sediment chemistry approach is based on a comparison of concentrations of metals in contaminated sediments with those in reference, uncontaminated sediments.

Advantages:

- can be implemented using available data;
- because of its simplicity, it has minimal data requirements;
- does not require toxicity testing or detailed chemical reasoning.

Disadvantages:

- difficult to define reference sediments;
- highly site-specific;
- does not take bioavailability into account;
- difficult to defend.

2 Water Quality Criteria (WQC)

The water quality criteria approach measures the concentration of metals in the interstitial waters of sediments and compares the values with accepted water quality standards.

Advantages:

- makes use of well-established toxicological database.

Disadvantages:

- Assumes that exposure of sediment organisms is via interstitial water and that this is the main uptake route (i.e., does not take account of uptake of contaminant particles or uptake via food);
- difficult to measure interstitial water quality;
- does not relate to mixtures;
- does not relate to the sediment of interest;
- no use if there are no relevant WQCs;
- assumes that sediment infauna have the same sensitivity as other life.

3 Sediment/water equilibrium partitioning

This approach combines EPA (or other) water quality criteria together with equilibrium partitioning calculations to obtain sediment contaminant concentrations that give rise to water concentrations equivalent to the criterion.

Advantages:

- makes use of well-established toxicological database;
- makes use of organic carbon;
- makes use of chemical equilibria which are often well-known;
- efficient for determining which chemicals are likely contributors to toxicity.

Disadvantages:

- assumes that interstitial water is the main uptake route (i.e., does not take account of uptake of contaminant particles or uptake via food);
- some partition coefficients are uncertain;
- only strictly valid for some organic compounds;
- data do not relate to mixtures;
- assumes that sediment infauna have the same sensitivity as other life;
- does not account for the presence of mixtures;
- produces a single SQG number, thus failing to recognise the fact that data from real sediments are too uncertain to support more than a range of values.

4 Sediment bioassay

Sediment bioassays may be used in two ways. Firstly, test animals may be exposed to a range of sediments from clean to heavily contaminated areas. The response of the organism considered to be unacceptable is related to the sediment composition, which is then taken as the standard. Secondly, animals may be exposed to a range of spiked sediments. Again, the response of the organism considered to be unacceptable may be related to the sediment composition which is then taken as the standard. In this second case a dose-response curve is developed.

Advantages:

- similar to WQCs: technically acceptable and legally defensible;
- good for identifying problem sediments;
- deals with synergism in real-world sediments;
- does not require prior knowledge of mechanisms of uptake.

Disadvantages:

- uncertainty over the cause of any effect;
- difficult to implement with a range of organisms;
- difficult to dose sediments;
- may not reflect chronic effects, and chronic effects difficult to predict from acute endpoints;
- massive amount of work to examine mixtures and dosages which can occur;
- no basis at present for extrapolating to no-effect concentrations in sedimentary communities.

5 Effect range- and effects level- approach (i.e., ERL/ERM and PEL/TEL)

Statistical analyses of matching chemical and biological data which have been used to determine the concentration below which effects are rarely observed, and the concentration above which the incidence of effects is elevated.

Advantages:

- can be used with any chemical constituent;
- can use existing databases;
- does not require prior knowledge of mechanisms.

Disadvantages:

- large amount of field data required;
- values are potentially sensitive to data used in calculation;
- cannot separate contaminant effects.

6 Apparent effects threshold (AET)

This approach uses field data on chemical concentrations in sediments and at least one indicator of bioavailability/bioeffects (e.g., sediment bioassays, benthic infaunal community structure, bottom-fish histopathological abnormalities, bioaccumulation). It determines the concentration of a particular contaminant above which statistically significant biological effects (relative to a reference site) are always expected.

Advantages:

- can be used to develop criteria for any contaminant using any effects measure provided it can be statistically evaluated;
- does not require prior knowledge of mechanisms;
- biological effects always occur above AET, so it is not uncertain.

Disadvantages:

- requires large database;
- can be influenced strongly by unknown toxic compounds;
- bioassay methods may not reflect chronic effects;
- no mechanism has been established to separate individual effects;
- not conservative (some toxic sediments will be missed)—as more data are added, the AET can only stay the same or increase (i.e., become less precautionary);
- does not establish safe levels;
- produces a single SQG number, thus failing to recognise the fact that data from real sediments are too uncertain to support more than a range of values.

7 Sediment Quality Triad

This approach is based on correspondences between three measures: sediment chemistry to determine contamination, sediment bioassays to determine toxicity and *in situ* bioeffects to determine alteration of resident communities.

Advantages:

- uses a combination of three different measures;
- does not require prior assumptions about mechanisms;
- can be used for any contaminant;
- accounts for both acute and chronic effects.

Disadvantages:

- requires a large database;
- can be strongly influenced by unmeasured compounds;
- statistical criteria have not yet been developed;
- methodology not yet fully developed.

8 Conclusions

It is apparent from the above that no single method for setting SQGs is free of problems. Several (e.g., background sediment chemistry; water quality criteria; equilibrium partitioning) are too simplistic because they either make no allowance for variations in bioavailability caused by differing sediment conditions, or assume incorrectly that all exposure occurs via the interstitial water. There is no doubt that the ingestion of sedimentary particles is a significant route by which adsorbed particulates exert toxicity, so methods which ignore this should not be considered further.

In theory, a much better approach would be to use sediment bioassays as the basis for setting SQGs, because they measure sediment toxicity to real sedimentary organisms and the contaminants present in a reasonably natural manner. However, it has to be recognised that spiked sediment tests do not mimic perfectly the bioavailability of some contaminants which have entered sediments naturally. Furthermore, there are only a few sediment toxicity test procedures available, with a relatively small number of taxa, and very few chronic test methods. This would severely

limit the reliability of SQG-setting based on safety factors because insufficient species and endpoints are currently available. This would in turn force the use of unrealistically high safety factors.

The Sediment Quality Triad is a more promising approach as it is based on the correspondence of chemical, bioassay and *in situ* biological data from a given site. However, the methodology for integrating data to give a reliable weight-of-evidence is not fully developed and the approach is probably too data-hungry and cumbersome to form the basis for operational sediment assessment for more than a handful of substances and locations.

The remaining methods are all variations of the co-occurrence concept. These approaches make use of all available data from many sediment studies, and they have the advantage that the detailed methodology has been fully worked out and to some extent validated. The Apparent Effects Threshold is the least attractive of the co-occurrence procedures because it is insufficiently precautionary. The other two main methods (TEL/PEL and ERL/ERM) are very similar and sufficiently conservative, with little to choose between them. However, the ERL/ERM is simpler to operate and has received the most validation. Of the available methods, it is therefore considered to be the most promising.

However, although the ERL/ERM approach therefore forms the soundest basis on which to develop SQGs for the UK, it is certainly not free from drawbacks, and these are discussed more fully in the next section. Until the ERL/ERM methodology has been fully validated for use with UK sediments and benthic organisms, it cannot be considered ready for operational deployment in this country. It will be important to establish that North American SQGs are both protective and predictive in local UK sediments and with tests of local fauna. The only way to do this is to analyse data from samples for which there are matching contaminant and biological data. It will be important to establish that samples in which no SQGs are exceeded are non-toxic; that the incidence and degree of toxicity increases with increases in the number of SQGs exceeded and the degree to which they are exceeded; and that dose-response relationships observed in UK sediments mimic those reported for North American sediments.

ANNEX 5: TECHNICAL ANNEX ON NORMALISATION

NORMALISATION OF CONTAMINANT CONCENTRATIONS IN SEDIMENTS

This annex provides guidance on the application of methods to normalise contaminant concentrations in sediments.

1 Introduction

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 not able to bind contaminants. This dilution effect will cause lower and variable contaminant concentrations in the resulting sediment. Obviously, grain size is one of the most important factors controlling the distribution of natural and anthropogenic components in sediments. It is, therefore, essential to normalise for the effects of grain size in order to provide a basis for meaningful comparisons of the occurrence of substances in sediments of varying granulometry and texture within individual areas, among areas, or in time.

When analysing whole sediment (i.e., <2 mm fraction) for spatial distribution surveys, the resulting maps give a direct reflection of the seabed sediments. However, in areas with varying grain size distributions, a map of contaminant concentrations will be closely related to the distribution of fine-grained sediments, 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 grain size distribution can obscure trends. If samples used for a spatial survey consist predominantly of fine material, the influence of grain size distribution is of minor importance and may probably be neglected.

2 Normalisation Procedures

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

- a) Normalisation can be performed by relating the contaminant concentration with components of the sediment that represent its affinity for contaminants, i.e., binding capacity. Such co-factors are called **normalisers** (cf. Section 4). Simple contaminant/normaliser ratios or linear regression can perform normalisation. Another procedure takes into account the coarse fraction containing natural metal concentrations in the crystal structure before the normalisation is performed. Using multiple regression and also combinations of co-factors can be identified as normalisers.
- b) Isolation of the fine fraction by sieving (e.g., <20 µm, <63 µm) can be regarded as a physical normalisation to reduce the differences in sediment granulometric compositions 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 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.

3 Limitations of normalisation

Clearly, normalisation procedures may not apply equally well to all elements at all sites; especially important in this respect are elements that participate in diagenetic reactions. In cases where there is a lack of full understanding of the geochemical processes operating, care should be taken when normalising for grain size differences. These processes can create important natural enrichment of metals at the sediment surface, as a result of the surficial recycling of oxihydroxides or deeper in the sediment as the result of co-precipitation of the metals with sulphides (cf., e.g., Gobeil *et al.*, 1997), which cannot be accounted for by normalisation.

4 Normalisation with Co-factors

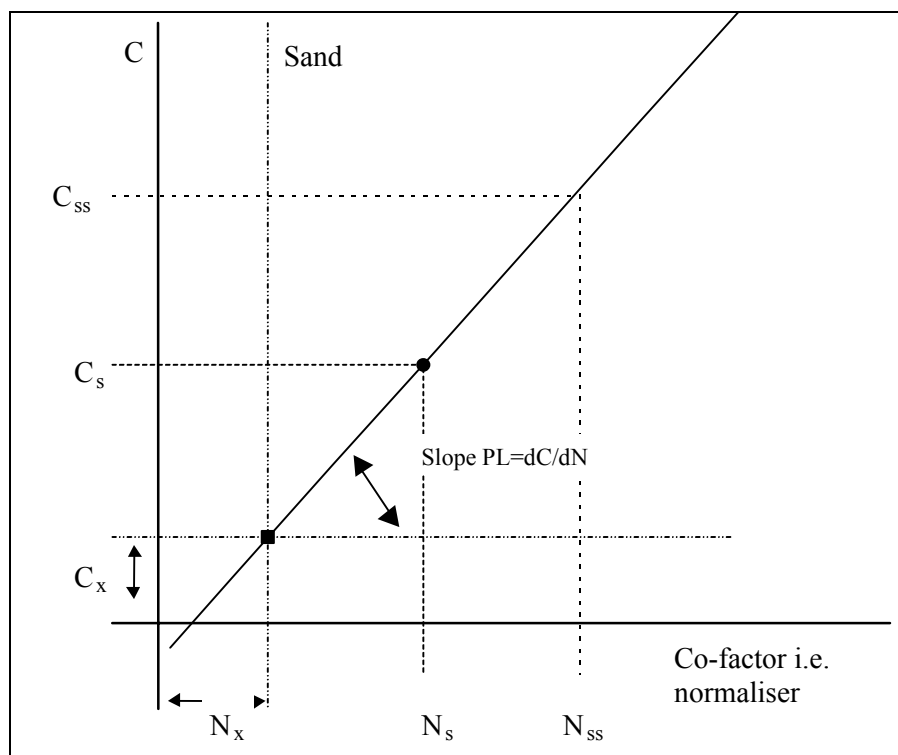
Normalisation by calculation with the content of a certain grain-size fraction such as $<2\ \mu\text{m}$ (clay), $<20\ \mu\text{m}$ and $<63\ \mu\text{m}$ can be used. This normalisation technique is based on the fact that the binding capacity of the sediments can be related to the content of fines (primary) in the sediments.

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 trace elements enriched in that fraction such lithium (Loring, 1991), these can also be used as a co-factor (secondary).

Both aluminium and lithium behave conservatively as they are not significantly affected by, for instance, early diagenetic processes or strong redox effects frequently observed in sediments. Problems may occur in cases where 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).

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. However, trace metals can be also normalised using the organic carbon content (Cato, 1977, 1989). Care has to be taken when normalising with organic carbon because organic matter is not a conservative component of sediments, for example, as concentrations may vary seasonally.

Figure A5.1. Relation between the contaminant C and the co-factor N (see text).



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 A5.1. 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 a regression between the contaminant and the co-factor will originate from that point. That means that regression lines of sample sets with a different contamination level and consequently different slopes will have this point in common (i.e., turning point). When this turning point is known, only one sample is required to estimate the slope. This allows determination of the contaminant content for any agreed (pre-selected) 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 clay 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 that 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 $<20 \mu\text{m}$ 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 on total and sieved samples, irrespective of 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 . Results can therefore always be reported with a standard deviation (Appendix B).

6 Considerations on co-factors

The **clay 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 variable. At present, other variables 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 much smaller than with total methods. Although normalising 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) the requirements of the programme are still 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 that usually is represented by **organic carbon**. Organic matter will also occur in the coarse fraction but is then still 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, that means 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 better defined than in the total sample. In addition, the nature of the organic matter may show spatial variation. For samples with low organic carbon content close to the detection limit, the 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 that there are no significant amounts of organic matter in coarse fractions, the proportion can be used as a normaliser. 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. As for aluminium with partial digestion (no HF) lower values are measured in the sand compared to total methods. This implies that partial digestion results in lower intercepts (turning point is closer to the zero). However, the partial digestion must be strong enough so that the clay will be totally digested, and the aluminium content measured remains representative for the clay. It was demonstrated that for fine material similar results are obtained for partial and total methods (QUASH/QUASIMEME).

In general, the correlation of the organic contaminants with organic carbon has 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 to or even below the detection limit. At present, for PAHs organic carbon is usually applied for normalisation. It should be recognised that due to the possible presence of undefined material, for example soot or ash, elevated PAH concentrations may occur in specific fractions that may have limited environmental significance. Although this needs further investigation, existing results indicate that PAH concentrations in the sieved fractions were not affected significantly.

8 Isolation of Fine Fractions for Analyses

Samples must be sieved over 2 mm mesh as soon as possible after sampling to remove large detritus and benthic organisms. Otherwise during further sample handling like storage, freezing or ultrasonic treatment, this 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 it should be considered to freeze-dry samples. In that case contamination and losses of contaminants during freeze-drying have to be checked. Air-drying is not appropriate due to high contamination risks. In addition, samples may be difficult to be disintegrated and mineral structures may be affected.

To isolate the fine-grained fractions, either the fraction <63 µm or <20 µm, a wet sieving procedure is required (freeze-dried samples will have to be resuspended using ultrasonic treatment). Sea water, preferably from the sampling site, should be used for sieving, as it reduces the risk of changes in the sample, i.e., losses through leaching or contamination. Furthermore, sea water supports the settling of fine particles after the sieving. If water from the sampling site is not available, then sea water from 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 water can be reused for sieving subsequent batches. Sediments should be agitated during sieving, in order to prevent clogging of the mesh and to disintegrate agglomerates of fines.

The currently most efficient sieving method pumps sea water over a sieve that is clamped onto a vibrating table. The water passing the sieve is led 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. Alternatively, small portions, 20–60 g, can be sieved by a manual system using an 8-cm sieve in a glass beaker placed in an ultrasonic bath. Particles can be isolated from the water passing the sieve by batch-wise centrifugation. The upper 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., a 200 µm mesh can facilitate the sieving process.

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

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

More information about the sieving procedures is available on a video produced by the QUASH Project (QUASH 1999).

Recommendations

- 1) For both temporal trend and spatial monitoring, it would be ideal to analyse samples with equal composition. This could be confirmed by determination of the co-factors Al, Li, OC and grain size distribution. However, this situation will not always occur, particularly not in spatial surveys.
- 2) New temporal trend programmes should be carried out by the analysis of fine sediments or a fine-grained fraction, isolated by sieving. Existing temporal trend programmes could be continued, provided that assessment of the data indicates that the statistical power of the programme 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 unacceptably high for sandy sediments, if both contaminant and co-factor concentrations are low, particularly when approaching detection limits. In that case, in order to draw reliable maps, alternative procedures, such as sieving, need to be used to minimise the impact of this error structure.
- 4) Variance arising from grain size differences can be reduced in a direct way by separation of a fine fraction from the whole sediment. Spatial distribution surveys of the concentrations of contaminants in separated fine fractions can be used to prepare maps, which will be much less influenced by grain size differences than maps of whole sediment analyses. There will still be some residual variance arising from differences in the composition (mineralogy and organic carbon content) of the sediments.
- 5) The natural variance of sample composition will be smaller in the fraction <20 µm than in the fraction <63 µm. Therefore, 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 nevertheless an acceptable compromise for both temporal trend and coordinated large-scale spatial surveys.
- 6) The preferred approach for preparing maps of the spatial distribution of contaminants in sediment consists of two steps: analyses of contaminants in fine sediments or in the fraction <63 µm followed by normalisation of analytical results using co-factors (cf. Section 4). 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. This should give the most consistent and comparable data sets over the ICES/OSPAR area. Maps of contaminant levels in fine sediments should be accompanied by mapping the co-factors in the whole sediments.
- 7) 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 grain size distribution of the original samples.

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Appendix A - 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 only rarely available. An alternative approach is to take one sample and to produce sub-samples with varying grain size distributions (Smedes 1997a, 1997b; QUASH, 2000). Both the fine and coarse sub-samples are analysed for contaminants and potential normalisers. In that 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 usefulness of potential normalisers.

Appendix B - Error calculation

To be filled in by Foppe Smedes after adoption of this document by ACME.

ANNEX 6: TEMPORAL TREND MONITORING (TTMON)

The theory behind the use of sediments as a tool in environmental monitoring is the knowledge that the finer particles in the sediment originate from the suspended particulate matter, and that these particles are the carriers of non-soluble contaminants. If needed, differences in the sediment matrix can be normalised between different samples, either by recalculation methods or select/transfer the samples to comparable composition.

Definition of TTmon:

Temporal trend monitoring is defined as repeated measurement/study of a certain parameter in a certain medium and at selected time intervals and using constant procedures. In this context, the medium is marine bottom sediments and the parameters are anthropogenic contaminants.

Objectives of TTmon:

Identify temporal changes of contaminant concentrations in sediments.

Methods to use:

Temporal trend monitoring of contaminants in sediments can in principle be executed by the following techniques:

- 1) Retrospective studies, i.e., studies of down-core concentrations.
- 2) Comparing concentrations from repeated surface sediment sampling at the same sites.
- 3) Comparing concentrations of repeated surface sediment sampling at different sites but within the same area.
- 4) Comparing concentrations in suspended particulate matter (SPM) collected regularly by sediment traps at the same sites.

Advantages/disadvantages of the different techniques:

Studies of *down-core concentrations* have been widely used when anthropogenic inputs to the environment should be described. In that case, down-core concentrations have been found to be very useful compared to other media as the sediment provides an integrated chemical picture over time and not a snapshot as, e.g., obtained from a single water sample. Thus, the down-core concentration technique is particularly useful when time trends over decades or centuries should be established. The technique can only be used on fine-grained sediments cored/sampled in areas with a continuous deposition. One should be aware that changes in sediment dynamics, changes in redox conditions, bioturbation as well as various diagenetic reactions may influence the concentration profile in the sediment.

When time trends of less than one decade should be studied, the down-core distribution technique is less useful and therefore not recommended. This is due to the difficulties of identifying the same time horizon between cores. However, laminated sediments are an exception to this statement. When laminated sediments cannot be used and time trends over short periods should be studied, the *repeated surface sediment sampling* technique is recommended. The sampling strategy can be based on either repeated sampling of fixed stations or on random sampling methods. The time interval between the sampling and/or the thickness of the surface sample taken is dependent on both the sedimentation rate and the sediment mixing rate. The former can be measured and the latter calculated.

In highly dynamic areas dominated by sandy bottom sediments, it is not possible to take surface samples representing a given time span of deposition. Instead surface samples from such bottom areas are to be considered as representing the current level of contamination recorded in the fine fraction of the sediments. No older information on contaminants is stored in these types of sediments. In these cases, time trend studies can be conducted by comparing average concentrations from repeated sampling of surface sediments. The sampling should be done within the same area but not necessarily on the same sites. By following either a *random sampling technique* or a *stratified random sampling technique*, the statistical probability can be ensured by different methods.

The *sediment trap* is a technique that has been used in trend monitoring in more limited areas. The traps collect material settling throughout the water column, but the influence of resuspension is strong for traps used in shallow areas with depths less than the maximum wave base depth. The advantage of the sediment trap method is the fixed time interval that can be used when collecting material. The technique may not give comparable results with bottom sediment sampling techniques. Another disadvantage of the technique is the costs of traps and that they may create problems and conflicts with other uses of the marine environment, e.g., trawling.

ANNEX 7: SEDIMENT-WATER INTERACTIONS OF CONTAMINANTS

Introduction

An important aspect of the environmental risk of sediment-bound contaminants is whether and to what extent they can exchange with the water phase. For a given contaminant this exchange is governed by the sediment particle-interstitial water distribution and a by combination of the water-side diffusive resistance and the resistance in the active sediment layer.

Generally, contaminants in the dissolved phase are considered bioavailable and thereby very important for the interpretation of biological effects measurements. For sediment-living organisms, the ingestion of contaminated sediment particles might be an important additional exposure route.

Therefore, to be able to estimate the environmental risk of sediment-associated contaminants it is very important to have information on:

- 1) the freely dissolved concentration in equilibrium with the sediment;
- 2) the desorption rate from the sediment;
- 3) the fraction in the sediment that is exchangeable with the water phase.

Newly developed methods can assist in this, as described below.

Freely dissolved concentration in equilibrium with the sediment

The concentrations in the freely dissolved fraction in a sediment-water mixture are not easily quantified. Due to the extremely low concentration, it is seldom possible to measure it directly.

The quantification is often influenced by the fraction of the contaminant associated with colloidal including dissolved organic matter. Alternative methods have recently been developed that may assist in the determination of the freely dissolved concentration. The first method is based on the work of Huckinson who deployed low-density polyethylene bags filled with triolein (a model lipid) in water systems. The uptake of this so-called SPMD is directly related to the exposure time, the exposure surface and the freely dissolved concentration, provided that the temperature and flow regime are constant. Exposing SPMDs to a mixture of sediment and water at constant temperature and dynamics for a fixed period will allow the establishment of a measure for the freely dissolved concentration. Care should be taken that the desorption rate is not limiting the uptake rate of the SPMDs. This is a matter of phase ratio and can be prevented by application of sufficient sediment or limiting the surface area of the SPMD.

A second method that has recently been introduced makes use of solid-phase micro-extraction (SPME) for sensing the fugacity³ in sediment pore waters. This method gives less chance for sediment exhaustion, as the uptake is very limited due to the small surface area. This method has been applied to rather contaminated sediments with promising results, but the final detection limits are presently not clear. A drawback is also the absence of sample clean-up possibilities.

Desorption rate from the sediment

The desorption rate from the sediment can be established by performing a so-called TENAX extraction. In practice, an amount of sediment containing about 100 mg of organic carbon is mixed with water and 1 g of Tenax (a polymer). The mixture is shaken for a selected period of time and allowed to separate or, for faster separation, be centrifuged. The sediment will settle and the Tenax will float on top of the water. When the mixing is performed in a separation funnel, the outlet can be used to remove the sediment suspension. The recovered Tenax can be extracted by shaking or Soxhlet extraction. Subsequent exposures to, each time fresh, Tenax will allow the construction of a desorption curve, and consequently the calculation of desorption rates. Cornelissen and colleagues, using this approach, demonstrated the presence of rapid, slow and very slow desorptive fractions in the sediment of some freshwater locations in The Netherlands. Apparently several forms of organic carbon with different sorption characteristics are present, however, they have so far not been identified.

Nevertheless, knowledge of the desorption profiles for different types of marine sediments will be of help in models that describe the transport and biological uptake of contaminants.

Fraction in the sediment that is exchangeable with the water phase

Considering that the rapid desorptive fraction is very important for uptake and transport considerations, the Tenax extraction is a possible approach for evaluating the extent to which a contaminant concentration in a sediment is environmentally relevant, at least on a short term. Measuring the desorption curves on a routine basis would give the most complete picture. Probably it is not practically feasible because it implies extensive analyses. A good alternative would be to measure the desorbable fraction after a fixed period of time, for example 24 hours. This could be developed into a standard method.

Importance for WGMS

Following the work on normalisation, WGMS recognised that investigations on the significance of contaminated sediments to water quality would be an important topic to focus on. The methods outlined above might represent a start for such work. Foppe Smedes informed the group that experiments are about to start in his laboratory. The impact of sediment contamination on the water phase will be investigated by exposing SPMDs to sediments of different origin and composition. It is intended to develop this method in the coming year and present some results at the 2002 WGMS meeting. It was suggested that a small intercalibration between the members of WGMS could help to show the value of the method. Depending on the progress Foppe Smedes will consider the possibility to execute such an exercise intersessionally for interested participants.

Information on the exchangeable contaminant fractions in sediments of the ICES area using the Tenax method will be a next step. This method is slightly more complicated and labour intensive and it is not yet clear how to interpret the results. It is suggested that information on the use of this method be collected intersessionally and discussed at the next meeting. The above methods focus primarily on organic contaminants. Recently similar methods as described here for organic contaminants have been described for metals. It would be useful to collect this information for discussion at next year's meeting.

References

- Huckins, J.N., Tubergen, M.W., and Manuweera, G.K., 1990. Semipermeable membrane devices containing model lipid: a new approach to monitoring the bioavailability of lipophilic contaminants and estimating their bioconcentration potential. *Chemosphere* 20: 533–552.
- Kees Booij, Hedwig M. Sleiderink and F. Smedes, Calibrating the uptake kinetics of semi-permeable membrane devices using exposure standards, *Environ Tox & Chem.* 17 (1998) 1236–1245.
- P. Mayer, W.H.J. Vaes, F. Wijnker, K.C.H.M. Legierse, R. Kraaij, J. Tolls and J.L.M Hermens, Sensing dissolved sediment pore water concentrations of persistent and bioaccumulative pollutants using disposable solid phase microextraction fibers. (reference will follow)

ANNEX 8: PAPERS PRESENTED TO THE LISBON MEETING OF WGMS

An Internet Database of Metadata on Seafloor Sediment Samples Held at European Institutions:
<http://www.eu.seased.net>

Smedes, F., deJong, A.S. and Davies, I.M., 2000. Determination of (mono-, di- and) tributyl tin in sediments. Analytical methods. J.Environ.Monit., 2000, 2, 541–549.

ANNEX 9: RECOMMENDATIONS

The Working Group on Marine Sediments in Relation to Pollution [WGMS] (new Chair: F. Smedes, The Netherlands) will meet at a venue in Spain on dates to be decided in 2002 to:

- a) review and revise intersessionally the Technical Annex on metal analyses in sediments and prepare this for WGMS 2002;
- b) produce intersessionally an inventory of national sediment quality criteria values and a report on how they are derived and present them for review and comment for the 2002 meeting of WGMS;
- c) review and report on a paper on Normalisation methods produced by Michael Kersten;
- d) intersessionally work on an Appendix on error calculation to the Normalisation Technical Annex;
- e) produce an inventory of national procedures for the implementation of temporal trend monitoring of contaminants in sediments;
- f) continue the work initiated on sediment dynamics of importance to temporal trend monitoring;
- g) intersessionally consider the EU Water Framework Directive (WFD) and compile national strategies for implementation of the WFD, particularly in relation to sediments. (We foresee that this will be a major topic in the future of WGMS);
- h) continue the work initiated on temporal trend monitoring.

The group considers that a joint meeting with WGBEC would be appropriate in 1–2 years' time.

Countries not currently represented in WGMS should be encouraged to participate in future work.