

REPORT OF THE
Working Group on Marine Sediments in Relation to Pollution

Tromsø, Norway
24–28 March 2003

This report is not to be quoted without prior consultation with the General Secretary. The document is a report of an expert group under the auspices of the International Council for the Exploration of the Sea and does not necessarily represent the views of the Council.

International Council for the Exploration of the Sea
Conseil International pour l'Exploration de la Mer

Palægade 2–4 DK–1261 Copenhagen K Denmark

TABLE OF CONTENTS

Section	Page
1 OPENING OF THE MEETING.....	1
2 ADOPTION OF THE AGENDA.....	1
3 ACTIVITIES WGMS CAN PROPOSE TAKING INTO ACCOUNT THE CURRENT DRAFT OF THE REVISED JAMP.....	1
4 INVENTORY OF SEDIMENT QUALITY CRITERIA	2
5 INVENTORY OF NATIONAL TEMPORAL TREND MONITORING PROGRAMMES.....	2
6 FURTHER WORK ON SEDIMENT MONITORING GUIDELINES, GUIDANCE ON THE INTERPRETATION OF TREND MONITORING DATA, TAKING INTO ACCOUNT SEDIMENT DYNAMICS	3
7 DEVELOPMENT OF INDICATORS OF SEDIMENT CONTAMINATION	3
8 REVIEW OF NEW MONITORING PARAMETERS TO QUANTIFY THE BIOAVAILABILITY OF HYDROPHOBIC ORGANIC SUBSTANCES IN SEDIMENT	5
9 GUIDELINES FOR INTEGRATED CHEMICAL AND BIOLOGICAL EFFECTS MONITORING (WITH MCWG AND WGBEC).....	6
10 ICES ENVIRONMENTAL DATA REPORTING FORMATS.....	6
11 ANY OTHER BUSINESS	7
11.1 Comparison studies between total and partial digestion method for metal analysis	7
11.2 Co-factors of organotin contents in harbour sediments.....	8
11.3 SEDNET progress.....	9
11.4 Recent nutrient records in the Baltic Sea	9
11.5 Cadmium in suspended matter and sediments off the northeast coast of England.....	10
11.6 Activities related to the management of dredged material	10
12 RECOMMENDATIONS AND ACTION LIST	10
13 DATE AND VENUE OF THE NEXT MEETING.....	10
14 CLOSURE OF THE MEETING	10
ANNEX 1: AGENDA OF THE 2003 WGMS MEETING IN TROMSØ.....	11
ANNEX 2: TOR FOR THE ICES-WGMS 2002 MEETING.....	12
ANNEX 3: LIST OF AVAILABLE DOCUMENTS	14
ANNEX 4: LIST OF PARTICIPANTS.....	15
ANNEX 5: PEN PICTURES OF PARTICIPANTS.....	17
ANNEX 6: INVENTORY OF SEDIMENT QUALITY CRITERIA AND HOW THEY ARE DERIVED.....	18
ANNEX 7: INVENTORY OF NATIONAL SEDIMENT TREND MONITORING PROGRAMMES.....	48
ANNEX 8: SEDIMENT DYNAMICS IN RELATION TO SEDIMENT TREND MONITORING.....	56
ANNEX 9: MEASUREMENTS IN RELATION TO (BIO-)AVAILABLE CONCENTRATIONS OF CONTAMINANTS IN SEDIMENTS	67
ANNEX 10: OVERVIEW OF STUDIES PERFORMED IN CANADA.....	70
ANNEX 11: TWO COMPARATIVE STUDIES OF METALS IN GEOGRAPHICALLY DIFFERENT SAMPLES ANALYSED AFTER TOTAL AND PARTIAL DIGESTION	73
ANNEX 12: RECOMMENDATIONS.....	82
ANNEX 13: ACTION LIST.....	84

1 OPENING OF THE MEETING

The 2003 meeting of the Working Group on Marine Sediments in Relation to Pollution (WGMS) was opened at 10.00 hrs on 24 March. The Chair referred to the number of participants at the previous meeting and mentioned that a large number of participants (15) representing 12 countries were present.

Kristoffer Næs from NIVA welcomed the group to Tromsø. He introduced his colleague Anita Evenset who would be the local contact during the meeting.

The meeting was started by an opening speech from the Director of the Institute Dr. Salve Dahle who informed about the status of Akvaplan-Niva. The welcome speech was concluded by wishing the meeting a pleasant and productive week.

Anita Evenset informed about logistic and facilities available. Kristoffer Næs explained the social programme. This would consist of a bus tour along some fjords. The return to Tromsø would be on a big steamer. On board NIVA will invite the group for a dinner.

2 ADOPTION OF THE AGENDA

The Chair went briefly through the agenda and made an inventory of presentations prepared by the participants. No major adaptations to the agenda were necessary, except some presentations were added to any other business. In response to the remarks of ACME that more data on comparison of strong partial and total digestion methodology was necessary this was discussed under “Any Other Business” as well. The agenda is attached as Annex 1. The terms of reference for the meeting are attached as Annex 3. The list of documents of the meeting is at Annex 3 and the list of participants is at Annex 4, with their pen pictures at Annex 5.

On a voluntary basis rapporteurs were appointed for the different agenda items. Sections of the summary record were collected on Thursday evening and distributed among the participants. On Friday, the summary record, based on the notes of the rapporteurs, and the produced annexes were discussed.

Presentations

Participant	Agenda item	Title
Patrick Roose	6	Trend detection of PCB153 in the Scheldt Estuary and the Southern North Sea.
Philippe Mayer	8	Matrix-SPME of Hydrophobic Organic Chemicals to determine their (bio)availability
Foppe Smedes	8	Methodological concept to estimate bio-availability parameters for hydrophobic contaminants in sediments using solid phase samplers (SPS) made of silicone rubber.
Claude Rouleau	8	Factors influencing the trophic transfer of sedimentary contaminants in the benthic food web
Foppe Smedes	11.2	Co-factors for organotin compounds
Per Jonsson	11.4	Recent Nutrient Records in the Baltic Sea
Caroline Whalley	11.5	Cd transport from West Coast of England to the North Sea
Maria Jesus Belzunce	11.6	An integrated study for the management of dredged material in the ports of the Basque country
Kristoffer Naes	11.6	Norway launch action plans for clean up of contaminated harbour and fjord sediments

3 ACTIVITIES WGMS CAN PROPOSE TAKING INTO ACCOUNT THE CURRENT DRAFT OF THE REVISED JAMP

The WGMS discussed the implementation framework outlined in WGMS03-03-01 and WGMS03-03-02. The JAMP products to which WGMS could contribute and the manner are given in the table below.

JAMP Product	Specific input from WGMS
BA-4 (4.2 and 4.3)	WGMS can contribute, if required, to contaminant-related work on these topics.
HT-1c	Advice on monitoring strategies for contaminants in sediments is a continuing task of WGMS
HT-2	Advice as requested by ICES
HT-3	WGMS can play a role in the development and evaluation of BRCs related to sediments.
HT-4	Advice as required.
HT-5	WGMS considers that dredged materials are in fact sediments and therefore WGMS can play a role in this. However, in the view of the WGMS, QA guidelines are an integral part of any analytical methodology, so the division between dredged material and sediments is not clear.
HT-6	This topic is part of WGMS's work field.
HT-7	This topic is part of WGMS's work field.
HM-3	Advice as requested by ICES.
HA-1	WGMS can contribute, if required, to sediment-related work on these topics.
HA-2a	WGMS can assist in this task, and advise on and review the sediment-related products.
HA-2c	WGMS can contribute, if required, to sediment-related work on these topics.

4 INVENTORY OF SEDIMENT QUALITY CRITERIA

Sediment quality guidelines are becoming an increasingly important tool towards the management and possible regulation of the marine environment. Results from this topic can be of use 1) authorities that are developing standards for use in regulatory or management processes, and 2) to regional regulatory Commissions such as OSPAR and HELCOM.

Caroline Whalley presented the draft inventory on sediment quality criteria from WGMS 2002. At the WGMS 2003 meeting, WGMS updated and revised the document to take account of the changes that have been made over the year in this rapidly developing area. This document is attached as Annex 6.

Some countries (e.g., Canada, The Netherlands, Norway, Sweden) have developed environmental quality standards, but most attention is currently focused on standards for dredged material disposal. Therefore, these data have also been reported in the inventory. Several member countries are currently revising or producing action level approaches towards sediment quality guidelines. There can be quite a range in concentrations applied to action levels. This may in part be explained by analytical differences (size fraction analysed, analytical method applied), but there also may be local/regional variation.

It is recommended that the finalised document be submitted to OSPAR MON, HELCOM MONAS, SEDNET WG2 and the EEA. It is suggested that the document is revised in 2–3 years' time to reflect changes in this rapidly developing area.

5 INVENTORY OF NATIONAL TEMPORAL TREND MONITORING PROGRAMMES

At the 2002 WGMS meeting, a status of the national temporal trend monitoring programmes was compiled. This work was completed as far as possible in a subgroup consisting of Martin Mørk Larsen and Linda Tyrrell. For some countries information is missing, but this seems inevitable, and therefore it was decided to finalise this document regardless of the incompleteness. Intersessionally, ICES had contributed with an overview of data actually held in the database at ICES. This overview has been incorporated in this inventory. The final document is attached to this report as Annex 7.

The inventory contains a short explanation of the different temporal trend strategies available followed by a country-by-country walk through of planned monitoring programmes for the coming years.

WGMS recommends the following:

- 1) The annex should be submitted to OSPAR MON and HELCOM MONAS as a background document;
- 2) The pivotal point used for normalisation according to the normalisation guidelines is generally not determined in the available data sets. WGMS suggests that the individual countries try to incorporate these in the future monitoring programmes. Alternatively Pivotal Points can be estimated from existing data at ICES, and made available for OSPAR MON/HELCOM MONAS for use in evaluation of sediment data;
- 3) Data sets currently not reported to ICES should be made available as soon as possible for the use in MON 2003.

With respect to the extraction of pivot points from existing data, the Median Sum of Weighted Residuals regression as presented by Robert Szava-Kovats under agenda item 7 would be a useful tool as it can handle a maximum of outliers without affecting the slope.

6 FURTHER WORK ON SEDIMENT MONITORING GUIDELINES, GUIDANCE ON THE INTERPRETATION OF TREND MONITORING DATA, TAKING INTO ACCOUNT SEDIMENT DYNAMICS

WGMS was requested to continue the work initiated on temporal trend monitoring. It is suggested that in addition to agenda item 5 this work would include the continuation of the work initiated on sediment dynamics of importance to temporal trend monitoring. Dynamic processes affect the concentrations of contaminants in sediments, and it is important that they are taken into account when evaluating time trends in, or designing monitoring schemes for, the rather variable conditions found in marine waters. The work should help ICES to provide advice on the monitoring of temporal changes in sediment quality, as this will be the next issue to be considered internationally once the guidelines for spatial monitoring are agreed.

With regard to sediment dynamics, a sub-group consisting of Hanneke Gieske, Jean-Louis Gonzalez, Per Jonsson and Claude Rouleau produced a working paper on sediment dynamics of importance to temporal trend monitoring. Several physical, chemical and biological processes may influence the contaminant concentrations in sediments, and are therefore relevant for the interpretation of time trends, and in fact also for the design of monitoring schemes. Physical processes include erosion, resuspension, transport and deposition. These processes are driven by different forces, such as, e.g., isostatic land up-lift, tidal and wind-driven currents, density currents, etc. Chemical processes include early diagenetic processes, such as redox processes and authigenic formation of minerals. The biological process discussed here is bioturbation.

In addition there are several more features, such as, e.g., presence of ice-sheets, eutrophication and degradation of organic matter that may be relevant to include in a revised future document. Contributions are therefore welcomed.

The working paper attempts to address the importance of sediment dynamics when interpreting temporal trend data on contaminants in sediments by presenting examples from several completely different areas. At present, only the conditions in North Sea and the Baltic Sea have been considered so far. The working paper is attached as Annex 8.

Recommendations:

1. As the work done so far is considered relevant to different OSPAR, HELCOM and ICES groups, the annexed paper is recommended to be distributed as a working paper to encourage further input in order to improve the paper.
2. Contributions on other areas, such as the St. Lawrence Gulf and Estuary and the Bay of Biscay will be worked with intersessionally and drafted at the next WGMS meeting. Contributions also from other areas will greatly improve the paper, and are welcomed.

7 DEVELOPMENT OF INDICATORS OF SEDIMENT CONTAMINATION

Development of practical indicators for sediment quality is of paramount importance to display the results of environmental assessments to the general public. Because of the expertise represented in WGMS, it may be an appropriate platform for the development of such indicators to ensure the best possible scientific basis.

First we need to agree on the definition of an indicator. An indicator is a relative numeric result (of a parameter or group) that allows a summary judgement of the quality of the environment. Indicators can provide an accessible way to describe the quality of an ecosystem.

In a view on indicators Robert Szava-Kovats presented a procedure, which was essentially a regression method to find outliers above the background values for metals. He had developed a regression method that allowed up to 50 % outliers. Outliers have a detrimental effect on regression analysis with respect to sediment normalization. In addition, when analytical data comprise both regression variables, imprecision can vary greatly within the range of variables. Median Sum of Weighted Residuals (MSWR) regression is a tool for performing regression with a data set that may be outlier rich and which adjusts for imprecision in both variables [0 WGMS03-07-02]. As such the MSWR model may prove to be more effective in determining baseline concentrations while maintaining the integrity of outlying observations. The deviation from the regression was transferred into an enrichment factor, which could be seen as an indicator.

In the discussion that followed it was recognised that the presented method was useful for situations where background samples are present in the data set. Hanneke Gieske mentioned that it would not work in the North Sea as she starts from the assumption that every surface sample is, or can be, contaminated. Background values then have to be deducted from samples taken from cores.

The enrichment factor Szava-Kovats uses could be seen as a kind of indicator to identify most contaminated spots in a designated area. Since the background can vary spatially, the enrichment factor is not automatically valid for spatial comparison. Secondly, it is depending on the binding if the enrichment factor has toxicological relevance.

Although such procedures as described above are not found ideal to represent a risk indicator, the advantage is that they can be applied to data from past and present, certainly in relation to time trends. For the future, risk-related indicators should be developed. Also measurement technology may need to focus on that aspect of indicators. This led to the approach suggested below, which is an attempt to have a matrix-independent indicator with a direct relation to criteria. At present this applies only for hydrophobic organic compounds (HOCs).

Development of a universal indicator

An indicator should permit strong protection of biota from hazardous substances, but developing indicators on a sound scientific basis is not an easy task. It is simply not possible to sum contaminant concentrations as each individual compound has its own risk level. Having an indicator for each individual compound is not relevant either since otherwise the concentration value may as well be used.

A simple way of creating an indicator could be to report the ratio between the measured content and a set quality criterion, e.g., "above 1 is poor quality and below 1 is good quality". These ratios could be summed to provide an indicator value. However, such an approach could allow the absence of some compounds to compensate for another whose value is higher than the safety threshold, which does not seem logical from a toxicological point of view.

A suggested methodology

Building on the work on availability (agenda item 8), it was suggested that a reference phase could provide a way of deriving an indicator. As currently WGMS has most experience of reference phases developed for hydrophobic organic compounds (HOCs), the discussion focused on these contaminants. For HOC's, it is thought that the availability or the "pressure" (fugacity) of compounds to escape from a medium can provide a useful measure of environmental condition. A reference phase can be used to turn this measure into the numeric value required for an indicator.

A reference phase is like a thermometer that measures the tendency of heat to escape a system. A reference phase assumes the fugacity of the medium with which it is equilibrated. As such it is like a finger that feels that beer has a lower temperature than water in the swimming pool, without knowing the temperature as a number. Likewise a reference phase can be used to "feel" that one site is more contaminated than another.

Development of using a reference phase for an indicator must start with some way of scaling the measurements. The most logical way to calibrate would be to equilibrate the reference phase with conditions/concentrations in the medium for which the quality guidelines were set or developed at the level of criterion. So every measurement with a reference phase that is higher than measured under these standard conditions is above the norm. Knowing that most quality criteria were initially set according to dissolved water concentrations, the content in the reference can be calculated from that value if the equilibrium partition coefficient of the reference phase with the water phase is known. Of course this can be reversed (see agenda item 8) and the dissolved concentration can be calculated and compared with the quality guidelines or used for monitoring purposes.

A particular advantage of the method is that the reference phase is not restricted to one medium. The reference phase can be equilibrated with every medium, and consequently every medium can be recalculated to a concentration in the water phase. By “every medium”, we mean sediments (in any composition); air and potentially also tissue (such as homogenised mussels or fish) provided that equilibrium can be attained before degradation of tissue occurs. Alternatively, the possibility might be considered to use implants *in vivo*.

Working with concentrations in a reference phase is a practical approach, but a more widely understood approach might be to apply a concentration in the water phase. In such an approach it seems that ultimately only a criterion for one medium is required. However there are still a lot of compounds with their own criteria.

Concluding this agenda item, it was realised that the approach using a reference phase would need further development prior to routine use. For other approaches it was suggested that participants investigate their own data and apply the ratio approaches mentioned above (relations with BRC and other criteria) and in the previous meeting. Participants then report back to the group next year with a view to advising MON on how to proceed. Participants were also requested to collect approaches used by other organisations.

Depending on the progress of the availability work (agenda item 8) the usefulness of reference phases for indicators can be evaluated further. Similar approaches could also be considered for metals.

8 REVIEW OF NEW MONITORING PARAMETERS TO QUANTIFY THE BIOAVAILABILITY OF HYDROPHOBIC ORGANIC SUBSTANCES IN SEDIMENT

Measuring the bioavailability of hydrophobic contaminants in sediments was again discussed during this meeting. Generally, monitoring organisations and regulatory bodies determine the total concentration levels of contaminants in sediments. These total concentrations quantify the amount present in the sediment, however, they do not describe what is available, e.g., for biotic uptake.

Recently, new measurement approaches have been developed that are based on diffusive sampling within sediment (suspensions). The new developments were presented to the group in the form of two presentations (listed under agenda item 2) and the group discussed this relatively new field during the plenary discussions. The general agreement is that this is considered to be a very promising new field. It could have important implications for monitoring programmes in the future.

The group should continue working on this and it needs to be backed by data. A sub-group (Ph. Mayer, F. Smedes, K. Næs and P. Roose) further discussed the technical aspects of this work and concluded that the methodology can be operated in two different ways that yield two different measurement endpoints. These were tentatively defined as the **freely dissolved concentration** and the **water exchangeable sediment concentration**. The subgroup also discussed the technical aspects of measuring these endpoints and the implications for monitoring. The outcome of this was discussed in plenary and a summary is given in Annex 9.

Similar approaches are likely to become available for the release of heavy metals from sediment and the group should actively follow up on this. A suggestion was to invite Dr. Zhang, a renowned expert on this topic, to give a presentation at next year's meeting.

In relation to the bioavailability and uptake of metals by organisms, Claude Rouleau gave a presentation on his work on the trophic transfer of metals in large benthic predators. In environments with low dissolved metal and/or organometal concentrations, the concentration in benthic fauna of lower trophic levels is proportional to that of the sediment, whereas uptake via food is the main accumulation route for higher predators. Accumulation of some metallic compounds, such as methyl mercury, through successive trophic levels can result in biomagnification, which is an increase of a contaminant concentration with increasing trophic level. This phenomenon may be of concern for both marine ecosystems (toxic effects exacerbated in top predators) and human consumers (more than permissible levels of a contaminant in seafood).

Unlike HOCs, there is no straightforward method, such as the correlation between K_{OW} and lipid-based concentration, to estimate the uptake of metals and organometals in marine organisms. The wide range of their chemical and environmental properties and the fact that the way organisms physiologically “handle” metals and organometals greatly differs from one species to another singularly complicate the task of assessing the transfer of sedimentary metals and organometals in the benthic food chain.

In his laboratory, Claude Rouleau measures the pharmacokinetic parameters of uptake, distribution, and elimination of single dietary doses of radiolabelled metals and organometals with techniques such as *in vivo* gamma counting and whole-body autoradiography. The measured values of the pharmacokinetic parameters are then used to model the long-term uptake of the metal or organometal studied.

Claude Rouleau had prepared a document (see Annex 10) with examples that show that the monitoring of metals and organometal levels in marine biota is far from being straightforward. Numerous factors must be taken into account and it would be advisable to further investigate and list these factors in order to help the interpretation of biomonitoring data, with the goal of providing policy-makers with sound scientific advice. Since Claude Rouleau was the only member in the group with expertise on this field, only a clarifying discussion was possible. The group recognised the importance of this work that could help to identify parameters that affect the release of metal when sediment would be ingested. However it was also questioned whether it would be inside the scope of the WGMS. Nevertheless it contributes to the understanding of fate and pathways of metals. The document with the examples was included for information as Annex 10.

9 GUIDELINES FOR INTEGRATED CHEMICAL AND BIOLOGICAL EFFECTS MONITORING (WITH MCWG AND WGBEC)

In relation to the JAMP, WGMS has been asked to supply guidelines for integrated monitoring. The aim of this work is to get a measure of the quality of the environment. However, within WGMS there is limited experience in applying such an approach, so this text is aimed at outlining the types of information, data and data interpretation required, as a starting point. There are a number of approaches available, such as Chapman's sediment quality triad approach, but as yet there is no generally accepted way forward. The following questions need to be considered:

- a) What is to be achieved by the monitoring? e.g., time trend; quality status; impact of management measures. This purpose will affect the data required and desired outputs, and other documents specify the need for statistical advice in ensuring that the sampling frequency, etc., will be sufficient to see if the measurements will be significant.
- b) What is to be achieved by integrating the monitoring? e.g., better understanding of processes, quality status, and (impact of) management measures.
- c) Which organisations have experience of integrating their programmes?
- d) Advice on what to do with data collected under programmes for, e.g., fish disease, biological effects and chemical monitoring is required. Collection of such data from the same station is possible, but then statistical treatment of the data needs to be used in a meaningful way. How to link these different measures in a statistically powerful way? As scientists, we might see an association between fish disease and contaminant concentrations at a particular station, but how can we more formally show whether there is a relationship?
- e) Advice is required, e.g., to collect samples at the same time from the same place, and how accurately this should be achieved (e.g., sediment samples in a grab but benthos/fish in a trawl from a larger area).
- f) Which procedures are the same and can be merged, and how can (must) interpretation be merged?

In the discussion, K. Næs noted that under the methods currently applied under JAMP (e.g., total concentrations) it may be difficult to find an association between chemistry and biological effects. In some work he had done, effects on a community could be related to PAH concentrations. In general, it is very difficult to find causal links between effects and contaminants, except in specific cases, e.g., TBT and imposex.

Members of WGMS should take this agenda item forward next year, and encourage members to bring forward information that will assist in this topic. F. Smedes and P. Roose will be attending WGBEC 2003 and hope to make an inventory of sediment monitoring and biological effects techniques, which may be integrated according to existing knowledge. K. Næs and M. Jesus Belzunce will collect information on integrated monitoring approaches as input to next years meeting.

10 ICES ENVIRONMENTAL DATA REPORTING FORMATS

The new system for Integrated Environmental Data Reporting Formats was presented by Jørgen Nørrevang Jensen from ICES. After this presentation, a subgroup consisting of Foppe Smedes, Martin Mørk Larsen, Patrick Roose, Jean-Louis Gonzalez, and Jørgen Nørrevang Jensen discussed the requirements for data concerning contaminants in sediment in the new ICES Environmental Reporting Format. Jørgen gave a short introduction to the information on the ICES website.

The group concentrated on the issue of pivotal points to be used in normalisation since this constituted the only major change in the reporting requirement that the group could envision. The group discussed the various ways to incorporate this information so that future assessment could be optimised.

The group recommended the following changes/additions in the new reporting format:

1. An extra field (PIVOT) should be added on the parameter record enabling the data submitter to fill in the pivotal point for the actual area and parameter (e.g., Al);
2. An extra field (PIVMT) should be added to the parameter record to indicate that the pivotal point has been calculated based on own data (C) or taken from an authorised list for the actual area (Foppe's list);
3. An extra code should be added to the PARAM field (PSAND);
4. An extra field should be added at the parameter record (SDERR) allowing the submitter to give the error of the actual measurement.

Alternative suggestion:

1. The codes for the PARAM field should be expanded with the following codes:
 - PIVXX, for the pivotal point for the substances XX, e.g., Al, based on an authorised list (Foppe's list);
 - PSNXX for the pivotal point for the substance XX based on measurement.
2. An extra field should be added at the parameter record (SDERR) allowing the submitter to give the error of the actual measurement.

Add. 1. The various methods for preparing the sand fraction for measurement of the pivotal point are covered by the link to the methods record.

11 ANY OTHER BUSINESS

11.1 Comparison studies between total and partial digestion method for metal analysis

At the 2002 WGMS meeting in San Sebastian, Carla Palma presented results obtained from the analysis of QUASH samples. Marine and estuarine sediments in different fractions (total, > 63 µm, < 63 µm, between 20 µm and 63 µm, and < 20 µm) were tested with total and partial digestion for trace metals using AAS. The results show that for most metals the concentrations were very similar, except for Al in coarse material. Also, it was remarkable that for Li and Ni the results obtained with strong partial digestion were higher than those obtained when using HF. Five replicate analyses were performed and the results are presented in Annex 11.

In response to the above, an investigation was carried out intersessionally between two laboratories (Instituto Hidrografico and RIKZ) to determine whether the abnormalities for Ni and Li could be clarified by further analyses. All samples were digested using total and partial methods by IH and analysed by AAS at IH (P) and by ICP-MS at RIKZ (NL). For all the elements the results obtained were very similar to previous work. For Ni a slight tendency to higher results in partial compared to total digests was observed with the samples analysed by AAS and sometimes with samples analysed by ICP-MS. Like the previous test also this time for Li, partial digest produced higher results than the total digest with AAS and ICP-MS.

To show the geographical factor in the comparison of total and partial digestion, data produced by RIKZ (partial) and the Baltic Sea Research Institute in Warnemünde (HF) were presented. Both laboratories analysed the same samples originating from the DIFFCHEM project from 1995. These data are plotted against the clay content determined by a physical measurement (Pipette method) in Annex 11 also. Although both methods did not always show the same contents, the differences are not obviously connected to the digestion methodology. Often the partial method resulted in slightly higher results compared to the HF digestion. Only for metals like K and Al, and when a large amount of coarse material is present, does the use of HF lead to higher contents. However when the fine material is dominating, similar values are obtained by both methods.

It can therefore be concluded that in samples from Portugal analysed in one laboratory no obvious differences are observed between the metal contents except the one mentioned above. Using different laboratories differences are apparently present but for these data partial digestion often shows higher results, except for the coarse samples. The

results do not allow identifying if this is caused by a systematic measuring error or an effect of the different matrix level that may be present in total digests compared to partial.

11.2 Co-factors of organotin contents in harbour sediments

Foppe Smedes presented research carried out at RIKZ to investigate what the best co-factors were for the correction of butyltin contents for differences in sediment composition. Therefore, five sediment samples were taken at locations with different pollution history and one at a dumpsite for low-contaminated harbour sludge. Organotin compounds (for example, mono- and di-heptyltin and tripropyl) were added to sub-samples. Two of these were prepared in duplicate to which also butyltin compounds were added. The samples were actively equilibrated on a tumbler for 3 months and subsequently separated in 6–9 fractions through sieving and differences in settling velocity, to obtain samples with a wide range of properties. All fractions were freeze-dried and analysed for co-factors and organotin compounds. By evaluation of the results through correlation, Organic Carbon (OC) and Nitrogen (N) were found to be the most appropriate co-factors (other co-factors examined were Al, Li, LOI and clay content). Figure 11.2.1 below shows an example for the relation obtained in the sample from the Nieuwe Waterweg (Rotterdam). OC is suitable when samples in the normal grain-size range are evaluated.

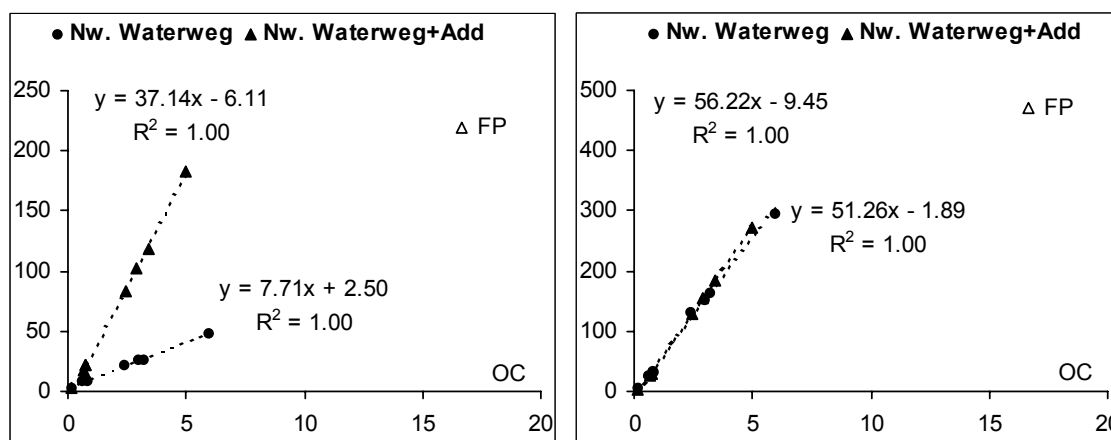


Figure 11.2.1. Relation between organic carbon content and Tributyltin (left) and Tripropyltin content in two duplicate samples from Nieuwe Waterweg (Rotterdam). Results indicated by triangles are from the sample with added TBT. Tripropyltin was added to both samples.

The figure also shows an open triangle representing a fraction of black coarse material with lower density than sand. In cases where coarse fractions become dominant, results indicated that N is a more suitable co-factor. The coarse fractions demonstrated a slow uptake of added compounds, which suggests that in those fractions the exchange of organotins with the water phase is limited. Therefore corrected concentrations of fine sediment fractions are a more accurate measure of the actual quality of the aquatic system.

Because the floating coarse (organic) material occurring in sediments shows lower contents when expressed on organic carbon and slower uptake than the fine fractions it might be considered to remove it by sieving, prior to analyses.

During the discussion Per Jonsson remarked that considering the relatively constant relation between N and OC, it seems that the organic matter was in the same state of degradation. F. Smede responded that for all samples there was likely no fresh organic matter present and it was certainly not dominating. The N-OC ratio was however not the same for all locations either because the origin of the organic matter or the degradation stage is different. Altogether it could be concluded that the N-OC ratio is a valuable parameter for interpretation of data.

K. Næs remarked that in field samples from shellfish areas they had not observed a correlation between organotins and organic carbon. F. Smedes answered that in field samples often contaminants are not always at the particles with the highest affinity as in such samples equilibrium is not always evident. The good correlations were simply the effect of equilibration before studying the relations. In this way compounds were allowed to distribute according to the affinity. Only in equilibrium the “fugacity” (see agenda item 8) is the same for all particles and a good correlation can be obtained.

The report on this work, available to the participants, is still a draft and therefore not annexed to this report.

11.3 SEDNET progress

SEDNET is a European Sediment Research Network, financially supported by European Commission from 2001 to 2004. The main and final deliverable is to produce guidance for integrated and sustainable sediment management (SSM), from local to river basin level.

In order to effectively achieve this aim SEDNET is structured in six working groups (WG), which combine people working on different technical and socio-economic aspects of sediments:

- WG1 Site investigation and characterisation
- WG2 Contaminant behaviour and fate
- WG3 Sediment treatment
- WG4 Planning and decision-making
- WG5 Risk management and communication
- WG6 Financial and economic aspects

The action plan mentions about two meetings per WG and per year plus an annual plenary Conference.

An important aim is to achieve fluid communication and information exchange between people dealing with sediments (scientists, environmental agents, politicians, users...) in order to know WHO is working, WHERE, on WHAT and HOW.

The main SEDNET deliverables are:

- methodology harmonization(*);
- production of guidelines(*);
- development of common proposals and projects.

(*) the existing documents already produced (or gathered) by WGMS could be taken into account.

During the meeting the group took notice of the progress on the SEDNET programme and identified links with WGMS. Several questions emerging in SEDNET work, especially in WG1 and WG2, have been discussed for years in WGMS. It seems useful to communicate ICES work to SEDNET as the progress report of SEDNET does not mention the work of ICES, OSPAR, or EEA. WGMS could contribute by, at least, the transfer of information and knowledge on several questions/problems identified by SEDNET.

To a certain extent there is communication but not on a formal basis. In 2002 the SEDNET Coordinator participated in the WGMS meeting held in San Sebastian. Some members of WGMS are actively involved in SEDNET works: preparation of the SEDNET proposal draft; 1st SEDNET Conference participation; participation as core group members in WG1. Furthermore, Foppe Smedes will attend the 2nd WG2 workshop in Berlin (3–5 April) and Maria J. Belzunce is planning to attend (if the financial support is arranged) the 2nd WG1 in Hamburg next April (25/27).

Considering the overlap, it is recommended that, where possible, the links between WGMS and SEDNET should be strengthened and therefore the participation of WGMS members at SEDNET meetings and vice versa is strongly encouraged.

11.4 Recent nutrient records in the Baltic Sea

Per Jonsson made a short presentation of the recent nutrient history in the Baltic Sea. In the mid-1990s the nutrient concentrations decreased and the conclusion was that remedial measures to reduce the discharges had been successful. However, recent assessment of nutrient data showed that this conclusion was premature. The storage of phosphorus in the entire water mass continued to increase in the late 1990s. Nitrogen showed a constant storage during this period

although the inorganic nitrogen content decreased in the deep water by a factor of almost 10, most likely due to a rapid denitrification in 1998–1999. The inorganic phosphorus content showed a gradual 40 % increase, caused by mobilisation from the sediments. These dramatic events were started after a wind-induced major salt-water inflow in 1993 emphasizing the importance of including natural processes when interpreting long-term nutrient trends.

11.5 Cadmium in suspended matter and sediments off the northeast coast of England

Caroline Whalley presented results of an investigation into cadmium and other metals in suspended matter off the northeast coast of England and the Dogger Bank. Recent oceanographic research has shown the existence of a seasonal transport pathway (“jet”) from the Tyne/Tees region out past the Dogger Bank towards the Skaggeirak. As elevated cadmium concentrations had previously been found in sediments at the Dogger Bank, the potential for the jet to transport cadmium was investigated. No evidence was found showing that cadmium was being transported in the jet. However, a correlation between chlorophyll *a* and cadmium in suspended particulates was observed in coastal and offshore waters.

11.6 Activities related to the management of dredged material

Maria J. Belzunce presented a Programme for an Integrated Study for the Management of Dredged Material and for the Environmental Surveillance on Dredged and Disposal Sites, being carried out on the ports of the Basque Country (North Spain). This study is commissioned by the Department of Transport and Public Works of the Basque Country. The main objective is to promote and to implement an environmentally well-done programme for the management of contaminated sediments from the Spanish ports. This programme includes chemical and biological control of sediments on dredged and disposal sites, as well as sediment dispersion and water quality studies in the disposal sites. A revision and improvement of the approach for the establishment of pollution levels of dredged material according to their potential effects on the marine ecosystem will be done. Plans for consultations and information to fishermen, port users and people affected by dredging and dumping activities are being done.

Kristoffer Næs gave a presentation of the plan Norway now has put into action for clean-up in contaminated harbour and fjord sediments. The background is that monitoring programmes have shown that harbour sediments and sediments in close vicinity to industrial installations might be highly contaminated. These sediments are considered a problem in terms of the risk they represent for spreading of contaminated particles and for uptake, accumulation and effects on organisms. By this they can also put restrictions on the consumption of local marine resources. The Norwegian authorities have therefore launched a comprehensive plan for clean-up in areas with contaminated sediments. The plan is divided into three phases and is based on the development of county-wise action plans. In phase 1 that is to be finalised within 2003, twenty-nine areas were chosen. The environmental status of the areas is summarised based on present knowledge, sources pinpointed as far as possible, possible high-risk sites identified, and a plan for phase 2 is developed. Phase 2 will span 2003–2005. In this period supplementary data are collected, the areas prioritised and the operational action plans developed. In phase 3 (2005–2009) the actual remedial action will be carried out. During phase 3 additional areas to be included are also considered.

Parallel to the initiatives described above, pilot projects are presently being performed. The pilot projects will fill identified gaps of knowledge. The objectives of these pilot projects are, for example, the effectiveness and cost of different technical solutions, quantification of diffuse sources, development of tools for risk assessment and decision support, etc.

12 RECOMMENDATIONS AND ACTION LIST

Recommendations and action list are added as Annex 11 and Annex 12.

13 DATE AND VENUE OF THE NEXT MEETING

The dates of the next meeting will be set by the chair in agreement with the host and with the intention not to overlap with MCWG and WGBEC. The venue of the meeting will be the Swedish Environmental Protection Agency, Stockholm, Sweden. The date was set for 1–5 March 2004.

14 CLOSURE OF THE MEETING

The WGMS thanked the organisers and hosts at AKVAPLAN-NIVA. The Chair closed the meeting at 15.00 hrs on 28 March 2003.

ANNEX 1: AGENDA OF THE 2003 WGMS MEETING IN TROMSØ

ICES Working Group on Marine Sediments in relation to pollution Tromsø, Norway, 24–28 March 2002

Agenda

- 1 Opening of the meeting
- 2 Adoption of the agenda
- 3 Activities WGMS can propose taking into account the current draft of the revised JAMP
- 4 Sediment Quality Criteria Inventory
- 5 Inventory of national Temporal Trend Monitoring Programmes
- 6 Annex to the sediment monitoring guidelines, Guidance on the interpretation of trend monitoring data, taking into account sediment dynamics.
- 7 Development of indicators of sediment contamination
- 8 Measurement of the potential bioavailability of contaminants in sediment
- 9 Guidelines for integrated chemical and biological effects monitoring (with MCWG&WGBEC)
- 10 ICES environmental data reporting formats
- 11 Any other business
 - 11.1 Further work on Metal analyses
 - 11.2 Co-factors of organotin contents in harbour sediments
 - 11.3 SEDNET progress
 - 11.4 Cadmium in suspended matter and sediments off the north east coast of England.
 - 11.5 Activities related to the Management of dredged material
- 12 Recommendations
- 13 Action list
- 14 Date and venue of the next meeting
- 15 Closure of the meeting

ANNEX 2: TOR FOR THE ICES-WGMS 2002 MEETING

2E04 The **Working Group on Marine Sediments in Relation to Pollution** [WGMS] (Chair: F. Smedes, Netherlands) will meet in Tromsø, Norway from 24–28 March 2003 to:

- a) review the relevant aspects of the implementation table of the OSPAR Joint Assessment and Monitoring Programme and indicate activities that could be proposed to be carried out by WGMS;
- b) further review and revise the inventory on Sediment Quality Criteria and the methodologies used to derive them;
- c) prepare inventories of national Temporal Trend Monitoring Programmes;
- d) prepare an annex to the sediment monitoring guidelines that provides guidance on the interpretation of trend monitoring data, taking into account sediment dynamics;
- e) continue work on the development of indicators of sediment contamination;
- f) review work on the measurement of the potential bioavailability of contaminants in sediment;
- g) consider and finalise draft guidelines for integrated chemical and biological effects monitoring (with MCWG and WGBEC);
- h) review the revised ICES Environmental Data Reporting Formats (Version 3.2) to ensure that all data relevant to monitoring contaminants in sediments will be submitted and provide comments to the ICES Marine Data Centre.

WGMS will report by 8 April 2003 for the attention of the Marine Habitat Committee and ACME.

Supporting information

Priority:	This group handles key issues regarding monitoring and assessment of contaminants in sediments.
Scientific Justification:	a) This is an OSPAR request for ICES to comment on the current draft of the revised JAMP, with a view to ICES advising OSPAR on where ICES work might contribute to the preparation of specific JAMP products. b) At the previous meeting, and intersessionally, sediment quality criteria (SQC) of various Member Countries were collected. The continuation of this work will ultimately allow a comparison of SQC and approaches for deriving them, applied in Member Countries. Such knowledge can possibly contribute to harmonization of SQC in the ICES area. c) Sediment quality assessments at the request of OSPAR or HELCOM will benefit from an overview of volume and qualities of Temporal Trend Monitoring activities in Member Countries. d) The proposed annex to the Sediment Monitoring Guidelines is an essential addition that will assist ICES in providing advice to others, e.g., OSPAR and HELCOM, on the interpretation of monitoring data with the view of detecting temporal changes in sediment quality. For this, sediment dynamics are of great importance as they affect the evolution of all sediments and should be included in the proposed Annex. e) Development of practical indicators for sediment quality is of paramount importance to display the results of environmental assessments to the general public. Because of the expertise represented in WGMS, it may be an appropriate platform for the development of such indicators to ensure the best possible scientific basis. f) Present monitoring methods are based on measuring the total contaminant concentrations in sediments. The resulting data do not necessarily represent the environmental risk due to the limited bioavailability of many contaminants in sediments. WGMS is an appropriate platform to discuss and investigate

	alternative methodologies for sediment assessments for future advice to ICES on taking bioavailability into account. g) This is required to promote integrated biological effects and chemical monitoring, to provide better assessment of the marine environment. h) This is a request from the ICES Secretariat.
Relation to Strategic Plan:	
Resource Requirements:	None required
Participants:	Subjects like bioavailability and SQC are of mutual interest to both WGBEC and WGMS. Periodic interactions between the groups and transfer of information are essential for efficient operation of both groups. Selected and interested members of the WGMS should participate in work of the WGBEC for the interaction and information transfer on the mutual issues such as SQC and bioavailability.
Secretariat Facilities:	None required
Financial:	None
Linkages to Advisory Committees:	ACME
Linkages to other Committees or Groups:	WGBEC, MCWG
Linkages to other Organisations:	OSPAR, HELCOM
Cost share	ICES 100 %

ANNEX 3: LIST OF AVAILABLE DOCUMENTS

Documents are numbered according to the following rule:<working group acronym>< year>-<agenda item>-<nr>

Ag.it.	Doc nr	Brief description
2	WGMS03-02-00	Agenda of WGMS 2002 meeting
	WGMS03-02-01	Terms of reference WGMS
	WGMS03-02-02	ACME report section 2002 Section 4
	WGMS03-02-03	Directions for rapporteurs
3	WGMS03-03-01	Framework for the implementation of Themes B, E, H, O, and R of the revised JAMP
	WGMS03-03-02	Potential ICES contributions to the framework for the implementation of Themes B, E, H, O, and R of the revised JAMP
4	WGMS02-04-00	Action and do list
	WGMS02-04-01	Draft 3 of “Inventory of Sediment quality criteria”
	WGMS02-04-02	Sediment quality criteria around the world, G.Allen Burton. Limnology 2002, 3, 65-75
	WGMS02-04-03	Implementation of bioavailability in standard setting and risk assessment, W.Peijnenburg, E.Sneller, D. Sijm, J.Lijzen, T.Traa, E.Verbruggen; J. Soils & Sediments, 2 ,(4) 169–173
5	WGMS02-05-00	Action and do list
	WGMS02-05-01	Draft of “Inventory of time trend monitoring of sediments undertaken”
7	WGMS02-07-01	Outlier-resistant errors in in-variables regression: anomaly recognition and grain-size correction in stream sediments. (2002) R.C. Szava-Kovats, Applied Geochemistry 17, 1149–1157
8	WGMS02-08-01	Measured pore-water Concentrations make equilibrium partitioning work-A data analysis (2003) R. Kraaij, Ph. Mayer, F.J.M. Busser, M. v/h Bolscher, W. Seinen, J. Tolls, A.C. Belfroid; Environ. Sci. Technol. 37, 268–274
	WGMS02-08-02	Methodological Concept to Estimate (Bio-)availability Parameters for Hydrophobic Contaminants in Sediments Using Solid Phase Samplers (SPS) Made From Silicone Rubber (2003) F. Smedes and A Luszezanec, Poster for SEDNET WG2, second workshop Berlin
10	WGMS02-10-1	Request to working groups for raw data
	WGMS02-10-2	The integration of environmental data reporting formats
	WGMS02-10-3	Integrated reporting Formats Version 3.2
	WGMS02-10-4	Presentation of Integrated reporting Formats
11.3	WGMS02-11.3a	Sediments and the European Framework directive, 2002, U. Forstner, J. Soils & Sediments, 2, 54
	WGMS02-11-3b	SEDNET progress report Year 1 (2002)

ANNEX 4: LIST OF PARTICIPANTS

Name	Address	Telephone no.	Fax no.	E-mail
Maria Jesus Belzunce	AZTI Oceanography and Marine Environment Department Muelle de la Herrera Recinto Portuario s/n 20110 Pasajes Spain	+34 943 00 4800	+ 34 943 00 4801	jbelzunce@azti.es
Hanneke Gieske	NITG-TNO P.O.Box 80015 2508 TA Utrecht The Netherlands	+31 30 256 4557	+31 30 256 4555	j.gieske@nitg.tno.nl
Jean-Louis Gonzalez	IFREMER Departement "Polluants chimiques" Z.P de Bregailon. 83507 La Seyne sur mer FRANCE	+33 494 30 48 56	+33 494 30 64 17	gonzalez@ifremer.fr
Per Jonsson	Stockholm University, Institute of Applied Environmental Research (ITMx), Laboratory for Aquatic Ecotoxicology S-106 91 Stockholm, Sweden	+46-8-674 74 72 Mobile +46-70-520 80 57	+46-8-674 76 38	per.jonsson@itm.su.se
Martin M. Larsen	Ministry of Environment & Energy Department of Marine Ecology Frederiksborgvej 399 DK-4000 Roskilde Denmark	+45 4630 1200	+45 4630 1114	mmml@dmu.dk
Philipp Mayer	Ministry of Environment & Energy Department of Environmental Chemistry & Microbiology Frederiksborgvej 399 DK-4000 Roskilde Denmark	Office: +45 4630 1200 Direct: +45 4630 1881	+45 4630 1114	phm@dmu.dk
Kristoffer Næs	Norwegian Institute for Water Research Southern Branch Televeien 3 N-4879 Grimstad Norway	+47 37 295067	+47 37 044513	kristoffer.naes@niva.no
Carla Palma	Instituto Hidrografico Rua das Trinas 49 1296 Lisbon Portugal	+351 21 3955119	+351 21 3960515	carla.palma@hidrografico.pt
Partrick Roose	Management Unit Mathematical Models of the North Sea – Royal Belgian Institute for Natural Sciences 3&23 Linierregimentsplein B-8400 Oostende Belgium	+32 59 700131	+32 59 70 49 35	p.roose@mumm.ac.be

Name	Address	Telephone no.	Fax no.	E-mail
Claude Rouleau	Fisheries and Oceans Canada Maurice-Lamontagne Institute 850 route de la mer P.O. Box 1000 Mont-Joli (Quebec) Canada G5H 3Z4	+1 418-775-0734	+1 418-775-0718	rouleaucl@dfo-mpo.gc.ca
Foppe Smedes (Chair)	National Institute for Coastal and Marine Manangement RWS/RIKZ P.O. Box 207 9750 AE Haren The Netherlands	+31 505 331306	+31 505 340772	<a href="mailto:f.smedes@rikz.rws.minve
nw.nl">f.smedes@rikz.rws.minve nw.nl
Robert Szava- Kovats	Dept. of Applied Ecology University of Tartu Lai 40 51005 Tartu Estonia			robszav@ut.ee
Linda Tyrrell	Marine Institute Marine Environment & Health Services Division Abbotstown Castleknock Dublin 15 Ireland	+ 353 1 822 8243	+ 353 1 820 5078	linda.tyrrell@marine.ie
Caroline Whalley	CEFAS Burnham Laboratory Remembrance Avenue Burnham-on-Crouch Essex CMO 8HA United Kingdom	+44 1 621787285	+44 1 621784989	c.m.whalley@cefas.co.uk
Jørgen Nørrevang Jensen	ICES Palaegade 2-4 DK-1261 Copenhagen K Denmark	+45 33 38 67 19	+45 33 93 42 15	joergen@ices.dk

ANNEX 5: PEN PICTURES OF PARTICIPANTS

Name	Pen picture
Maria Jesus Belzunce	A chemist working in the assessment of marine sediments as part of a Monitoring Programme along the Basque Coast, and the problematic of the dredged material. Currently is involved in the implementation of ecotoxicological analysis. Key words: marine sediments, metal contamination, and ecotoxicity.
Hanneke Gieske	A geologist, working on geochemical baseline studies of The Netherlands continental shelf and on geochemical research relating sources, transport and deposition of sand and mud and the effect of sediment dynamics on the distribution of contaminants.
Jean-Louis Gonzalez	A geochemist working on behaviour of contaminants in coastal environment (French estuaries - Mediterranean sea). Involved in geochemical modeling (development of speciation models and diagenetic models).
Per Jonsson	A marine sedimentologist part-time working at the Swedish Environmental Protection Agency and part-time as adjunct professor in recent marine sedimentology at Uppsala University. Main scientific interest in sediment and pollutant dynamics in the Baltic Sea.
Martin M. Larsen	A chemist, working with the Danish National Monitoring of biota and sediments. Special interest in metals but also in reporting of PAH, PCB, TBT results to ICES. Currently also involved in work on the implementation of the Habitat and Water Framework Directives in Denmark
Philipp Mayer	A senior scientist from the National Environmental Research Institute, Denmark. Working with the chemical analysis of organic contaminants and the development of new measurement approaches that are directed at contaminant availability.
Kristoffer Naes	Geochemist by profession. Has mainly been working with assessing impact on fjord and coastal waters of organic micro pollutants (PAHs, PCBs, dioxins, etc.) discharged from heavy industry. Has 20-year experience in the field. Is affiliated to the Norwegian Institute for Water Research, currently as research leader (head) of section working with micro pollutants in the marine environment.
Carla Palma	Chemist working in the Division of Marine Chemistry and responsible for the analysis on heavy metals in sediments and seawater in estuarine and coastal environmental programmes.
Partrick Roose	Has been working for more than 11 years in the field of marine environmental chemistry and is specialised in the determination of organic contaminants in the various marine matrices. He is currently head of the Marine Laboratory of MUMM and chairman of the OSPAR Working Group on "Substances in the Marine Environment" (SIME)
Claude Rouleau	Working in the Maurice-Lamontagne Institute, Fisheries and Oceans Canada. Interests include fate of metals, organometals, and hydrocarbons in sediment, with an emphasis on bioaccumulation and food chain transfer. Work with radioisotopic techniques, such as in vivo gamma counting and whole-body autoradiography. Modelisation of contaminants accumulation with pharmacokinetic models.
Foppe Smedes	Has worked for 30 years in analytical chemistry. In the last 15 years his work field has slowly changed to environmental research on mainly organic substances. In addition to this, he contributes more and more to advisory projects that turn monitoring data, through assessment, into advice to policy makers
Robert Szava-Kovats	Researcher at the Department of Ecology, University of Tartu, Estonia with a background in geochemistry and statistics. Interests include sediment and soil geochemistry, statistical modeling and analysis of compositional data.
Linda Tyrrell	Has been working for the past 4 years on the analysis of metals in marine sediments and biota (two years of which involved an MSc project on the development and validation of methods for the determination of 12 metals in deep sea sediment taken from the Rockall Trough, Atlantic Ocean as part of a baseline study).
Caroline Whalley	Environmental chemist at CEFAS Laboratory, Burnham-on-Crouch, UK. Interests include metals in suspended and surface sediments, metal transport by particulate phase, analytical quality control.
Jørgen Nørrevang Jensen	Data Scientist from ICES

ANNEX 6: INVENTORY OF SEDIMENT QUALITY CRITERIA AND HOW THEY ARE DERIVED

I INTRODUCTION

At the WGMS meeting in 2001, it was recommended that WGMS produce an inventory of national sediment quality criteria and the approaches used to reach such criteria.

Objective

Sediment quality guidelines (SQG) provide a method for assessing the quality of sediments, and may be used in classifying environmental quality or determining whether dredged material may be disposed of at sea. This inventory identifies the situation in member countries in 2002. WGMS can provide scientific advice on the approaches used, so that managers may take more informed decisions based on the use of such criteria.

Summary

A review of approaches used towards sediment quality guidelines (sometimes referred to as sediment quality criteria) was performed. Then those for the applications of environmental quality standards and dredged material disposal were considered. The general approaches taken by member countries are summarised in Tables A6.1 and A6.4. Where data are available for contaminant limits, these have been included in this report.

Most member countries currently do not have environmental quality standards (EQS) set in legislation for sediments. In these cases responsible authorities frequently use guideline values, which may be based on the OSPAR background reference concentration for that substance, or on locally derived background concentrations. However, several member countries are developing EQS values for sediments and more data should become available over the next few years.

In contrast, most countries do have legislative standards governing the disposal of dredged material at sea. Most member countries operate an action level approach to the disposal of dredged material, where “target” values are used to represent (near-) background concentrations and “limit” (or “intervention”) values represent the upper limit of acceptability above which action may have to be taken. Three countries use a case-by-case approach to dredged material assessment, but these are under review and are likely to be replaced by some type of action level approach.

For most substances considered, there is some consistency among the concentrations set for target concentration values. Ranges in limit values are much higher however, and this cannot generally be explained by differences in grain size. It seems more likely that the large differences between limit values in different countries instead reflect local conditions.

II REVIEW OF SOME METHODS USED FOR SETTING SEDIMENT QUALITY GUIDELINES

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;
- has minimal data requirements because of its simplicity;
- 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 because of the difficulties of identifying background sediments.

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;
- are of 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);
- 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 Ecotoxicological approaches to sediment quality criteria

Perhaps the most developed of the ecotoxicological approaches to sediment quality criteria have been produced by Long and McDonald (Long *et al.*, 1995; Long and MacDonald, 1998) in the U.S. Their data sets, which took a statistical approach in matching biological and chemical data from modelling, laboratory and field studies in North America, have since been developed to set sediment quality guidelines in a number of countries, notably the U.S., Canada and Hong Kong. Chemical concentrations only were used to derive effects range-low (ERL) and effects range-median (ERM) sediment quality criteria. However, calculation of Threshold Effects Levels (TEL) and Probable Effects Levels (PEL) values incorporated concentrations associated with both effects and no observed effects (Long and MacDonald, 1998).

Some work has been reported assessing the “accuracy” of sediment quality guidelines. ERL and ERM values were used to define concentration ranges that were: i) rarely (e.g., <10 %); ii) occasionally (usually ~25 %); or iii) frequently (usually ~70 %) associated with adverse effects (Long and MacDonald, 1998). To assist in the management of prioritisation of sediments, these authors (*ibid*) reported results from studies where multiple exceedances of ERMs were observed. Their data showed, for example, that 40–60 % of samples in which individual ERMs or PELs were exceeded proved to be highly toxic in amphipod survival tests. With respect to mixtures, where >10 ERMs (or >21 PELs) were exceeded, the probability of observing toxicity in amphipod survival tests was 74–88 %. Where concentrations of substances were below the ERL or TEL, the incidence of effects was generally below 16 % (Long and MacDonald, 1998). Such data provide confidence in effectiveness of the ERM and PEL approach.

In a recent paper, Burton (2002) emphasised that sediment quality guidelines should be used in a screening manner as part of a holistic assessment. This integrated approach is in accordance with the intended application of the action level guidelines currently being proposed. Balancing multiple “lines of evidence” concerning ecological assessment to aid decision-making, is the focus of recent discussions regarding “weight of evidence” approaches to environmental management of sediments (Burton *et al.*, 2002; Chapman *et al.*, 2002).

9 Discussion

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 are only applicable to non-benthic organisms.

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, potentially introducing 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.

10 References

- Burton, G.A. 2002. Sediment quality criteria in use around the world. *Limnology*, 3: 65–75.
- Chapman, P.M., McDonald, B.G., and Lawrence, G.S. 2002 Weight of evidence issues and frameworks for sediment quality (and other) assessments. *Human Ecol Risk Assessment*, 8 (7): 1489–1515.
- Ingersoll, C.G., Dillon, T., and Biddinger, G.R. 1997. *Ecological Risk Assessment of Contaminated Sediments*. SETAC Press, Pensacola, 390 pp.
- Long, E., MacDonald, D., Smith, S., and Calder, F. 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental Management*, 19 (1): 81–97.
- Long, E., Field, J., and MacDonald, D. 1998. Predicting toxicity in marine sediments with numerical sediment quality guidelines. *Environ Toxicol Chem*, 17 (4): 714–727.
- Long, E., and MacDonald, D. 1998 Recommended uses of empirically derived, sediment quality guidelines for marine and estuarine ecosystems. *Human Ecol Risk Assess*, 4 (5): 1019–1039.

III EXISTING APPROACHES IN MEMBER COUNTRIES

IIIa ENVIRONMENTAL QUALITY STANDARDS FOR SEDIMENTS

Summary

Currently, countries frequently compare their sediment data with those specified under OSPAR background/reference concentrations (BRC) (MON 00/5/Info.4-E). However, implementation of the Water Framework Directive (WFD) (Dir 2000/60/EC) is causing some member countries to review their existing approach, since it requires definition of 5 class levels (high status, good, moderate, poor and bad). An EU group, the Expert Advisory Forum (EAF), is examining Environmental Quality Standards (EQS) for priority substances, in line with requirements for WFD, and these EQS will define the boundaries between good and moderate status.

The approach for other classes has yet to be considered. However, the WFD defines high status for specific synthetic substances as close to zero and at least below the limit of detection of the most advanced techniques in general use. For specific non-synthetic substances, concentrations should remain within the range normally associated with undisturbed conditions.

A summary of the approaches towards environmental quality standards for sediments used in member countries is given in Table A6.1. See Tables A6.6–A6.14 for more detailed data applied in Canada, The Netherlands, Norway and Sweden.

Table A6.1. Summary of Environmental Quality Standards for sediments in ICES Member Countries.

Country	Legislation	Notes
Belgium	x	Data compared against OSPAR BRC
Canada	?	ISQG and PEL approach, from field data demonstrating associations between chemistry and biological effects
Denmark	x	Locally derived BCs from reference sediments (mainly for metals)
Finland	x	
France	x	Data compared against OSPAR BRC and locally derived BC from cored sediments
Germany	x	
Portugal	x	Data compared against OSPAR BRC
Netherlands	yes	2 class system (NEC and MPC) based on equilibrium partitioning or ecotoxicological data. See further notes below.
Norway	yes	5 class system. Data compared against local, surface sediment concentrations. See further notes below.
Ireland	x	
Spain	x	Data compared with international (e.g., USEPA) and locally derived BCs.
Sweden	yes	5 class system. BCs derived from cored sediments. See further notes below.
UK (England and Wales)	x	Data compared against OSPAR BRC; locally derived BCs in preparation

Notes:

x = standards not currently covered by legislation;
 ISQG = Interim sediment quality guideline;
 USEPA = United States Environmental Protection Agency;
 NEC = No Effect Concentration;

BRC = Background/reference concentration;
 PEL = Probable effects level;
 BC = background concentration;
 MPC = Maximum Permissible Concentration.

Most member countries currently do not have environmental quality standards for sediments set in legislation. In these cases responsible authorities frequently use guideline values, which may be based on the OSPAR background/reference

concentration for that substance, or on locally derived background concentrations. However, several member countries are developing EQS values for sediments and more data should become available over the next few years.

Table A6.2 shows the range in EQS values currently available. The range shown for the 5-class system used by both Norway and Sweden shows the lowest value given in that class to the highest value, providing an indication as to the range of concentrations that may be graded as, for example “class 4”. It can be difficult to compare between differing classification schemes, and this difficulty may be compounded as more countries adopt EQS values, depending upon the approach taken to determining environmental quality, protection of aquatic life, etc. However, broadly it can be seen that the Netherlands No Effects Concentration (NEC) and Canadian ISQG correspond to Classes 1–2 under the Norwegian and Swedish classifications. However, the ISQG values for benzo(a)pyrene and DDTs are somewhat higher, being closer to the Dutch MPC and classes 4–5 (the disparity in DDTs is unlikely to result from inclusion of *o,p'* isomers in the Canadian values). The Maximum Permissible Concentration (MPC) and PEL concentrations generally fall in Swedish class 4–5, but between class 2–5 in the Norwegian system, which appears to result from the large range covered by the Norwegian values.

Table A6.2. Summary of value ranges used for classifying sediments according to EQS values.

	Units	Norway and Sweden					Netherlands		Canada	
		Class 1	Class 2	Class 3	Class 4	Class 5	NEC	MPC	ISQG	PEL
As	mg/kg	≤10–<20	10–80	16–400	26–1000	>40–>1000	29	55	7.24	41.6
Cd	mg/kg	≤0.2–<0.25	0.2–1	0.5–5	1.2–10	>3–>10	0.8	12	0.7	4.2
Cr	mg/kg	<70–≤80	70–300	112–1500	160–5000	>224–>5000	100	380	52.3	160
Cu	mg/kg	≤15–<35	15–150	30–700	60–1500	>120–>1500	36	73	18.7	108
Inorganic Hg	mg/kg	*	*	*	*	*	0.3	10	*	*
Organic Hg	mg/kg	*	*	*	*	*	0.3	1.4	*	*
Hg	mg/kg	≤0.04–<0.15	0.04–0.6	0.1–3	0.27–5	>0.72–>5	*	*	0.13	0.7
Pb	mg/kg	<30–≤31	30–120	47–600	68–1500	>102–>1500	85	530	30.2	112
Ni	mg/kg	<30–≤33	30–130	43–600	56–1500	>79–>1500	35	44	*	*
Zn	mg/kg	≤85–<150	85–650	128–3000	196–10000	>298–>10000	140	520	124	271
Σ7 PCB	µg/kg	0–<5	0–25	1.3–100	4–300	>15–>300	*	*	(21.5) ³	(189) ³
B(a)P	µg/kg	0–<10	0–50	20–200	60–500	>180–>500	3	3000	88.8	763
EPOC ¹	µg/kg	0–<100	0–500	150–2000	700–15000	>3000–>15000	*	*	*	*
HCB	µg/kg	0–<0.5	0–2.5	0.04–10	0.2–50	>1–>50	0.05	5	*	*
Sum DDT	µg/kg	0–<0.5	0–2.5	0.2–10	1–50	>6–>50	*	*	*	*
p,p'-DDT ²	µg/kg	0	0–0.02	0.02–0.1	0.1–0.7	> 0.7	0.09	9	1.19 ⁴	4.77 ⁴
p,p'-DDE ²	µg/kg	0	0–0.2	0.2–0.7	0.7–2.5	> 2.5	0.02	2	2.07 ⁴	374 ⁴
p,p'-DDD ²	µg/kg	0	0–0.13	0.13–0.8	0.8–5	> 5	0.01	1	1.22 ⁴	7.81 ⁴

Notes

1) EPOC = Total persistent extractable organic chlorine

2) # = Values for Swedish 5-classes only.

3) Total PCBs

4) Total of *p,p'* and *o,p'* isomers

Further notes to Table A6.1 for individual countries

a) CANADA

Further details on Canada's approach to sediment quality guidelines can be found at <http://www.ec.gc.ca/ceqg-rcqe/English/Ceqg/Sediment/default.cfm> and data are presented in Table A6.6.

Sediment quality guidelines formulated on the basis of biological-effect data of sediment-associated chemicals are intended to be used as nationally consistent benchmarks. During their implementation, however, allowance must be made for the incidence of natural inorganic and organic substances in sediments. Adverse biological effects may be observed below measured chemical concentrations that are attributable to natural enrichment. However, management concerns over the potential for adverse effects of sediment-associated chemicals (particularly trace metals) must be practically focused on those chemicals whose concentrations have been augmented above those that would be expected to occur naturally. Therefore, the potential for adverse biological effects as indicated by the exceedances of SQGs must be evaluated in conjunction with other information such as the natural background concentrations of substances. In some management scenarios, it may also be necessary to consider concentrations of ubiquitous organic chemicals (i.e., the low level contamination of certain substances that are found throughout many environmental compartments) that are representative of reference or "clean" sites.

Guiding Principles

The following guiding principles for the development of Canadian SQGs for the protection of aquatic life are based on those adopted by the Canadian Council of Ministers of the Environment (CCME, 1991) for the development of Canadian water quality guidelines.

SQGs are numerical concentrations or narrative statements that are set with the intention to protect all forms of aquatic life and all aspects of their aquatic life cycles during an indefinite period of exposure to substances associated with bed sediments.

In deriving SQGs for the protection of aquatic life, all components of the aquatic ecosystem (e.g., bacteria, algae, macrophytes, invertebrates, fish) are considered, if the data are available. However, evaluation of the available data should focus on ecologically relevant species.

Interim SQGs (ISQGs) are derived when data are available but limited, and information gaps are explicitly outlined.

Unless otherwise specified, SQGs refer to the total concentration of the substance in surficial sediments (i.e., the upper few centimetres) on a dry weight basis (e.g., $\text{mg}\cdot\text{kg}^{-1}$ dry weight). However, sediments represent a complex and dynamic matrix of biotic and abiotic components that may influence the bioavailability of sediment-associated chemicals. When sufficient information is available to define the influence of any factor on the toxicity of a specific substance (e.g., TOC for nonpolar organic substances) (Swartz *et al.*, 1990; Di Toro *et al.*, 1991), the guidelines will be developed to reflect this relationship. Consideration of these relationships will increase the applicability of guidelines to a wide variety of sediments throughout Canada.

SQGs are refined as new and relevant scientific data become available. The refinement of these guidelines in the longer term will provide a means of ensuring their broader applicability.

References

- CCME. Canadian Council of Ministers of the Environment. 1991. Appendix IX — A protocol for the derivation of water quality guidelines for the protection of aquatic life (April 1991). In: Canadian water quality guidelines, Canadian Council of Resource and Environment Ministers. 1987. Prepared by the Task Force on Water Quality Guidelines. [Updated and reprinted with minor revisions and editorial changes in Canadian environmental quality guidelines, Chapter 4, Canadian Council of Ministers of the Environment, 1999, Winnipeg.]
- Di Toro, D.M., Zarba, C.S., Hansen, D.J., W.J. Berry, W.J., Swartz, R.C., Cowan, C.E., Pavlou, S.P., Allen, H.E., Thomas, N.A., and Paquin, P.R. 1991. Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environ. Toxicol. Chem.*, 10: 1541–1583.
- Swartz, R.C., Schults, D.W., DeWitt, T.H., Ditsworth, G.R., and Lamberson, J.O. 1990. Toxicity of fluoranthene in sediment to marine amphipods: A test of the equilibrium partitioning approach to sediment quality criteria. *Environ. Toxicol. Chem.*, 9: 1071–1080.

b) DENMARK

Sediment quality criteria have been requested under the Water Framework Directive, and it is expected that this will guide the development of such EQS in Denmark within the next few years.

c) FINLAND

Sediment quality criteria have been requested under the Water Framework Directive, and it is expected that this will guide the development of such environmental quality criteria in Finland.

d) THE NETHERLANDS

Table A6.7 shows NC (Negligible Concentration) and MPC (Maximum Permissible Concentration) environmental quality standard data for sediments in the Netherlands.

Derivations of ERLs and EQSs in the Netherlands (Traas, 2001)

Introduction

ERLs (environmental risk limits) are derived for different environmental compartments, based on observed or expected effects on species inhabiting these compartments, including effects from food chain exposure of predators (secondary poisoning). ERLs are used as scientific advisory values to set EQSs (environmental quality standards) by the government. When setting EQSs the government can take into consideration the advice of consulting parties and can take into account socio-economic factors. Table A6.3 explains the relationship between the different ERLs and EQSs: the EQS target value can be related to Action Level 1 in the classification system of some other countries.

Table A6.3. Comparison of terms used in the setting of ERLs and EQSs in the Netherlands.

Description	ERL	EQS
The NC (negligible concentration) represents a value causing negligible effects to ecosystems. The NC is derived from the MPC by dividing it by 100. This factor is applied to take into account possible synergistic effects.	NC, Negligible concentration. (air, water, soil, groundwater and sediment)	Target value (air, water, soil, groundwater and sediment)
A concentration of a substance in air, water, soil or sediment that should protect all species in ecosystems from adverse effects of that substance. A cut off value is set at the fifth percentile if a species sensitivity distribution of NOECs is used. This is the hazardous concentration of 5 % of the species (HC5).	MPC, maximum permissible concentration. (air, water, soil, groundwater and sediment)	MPC, maximum permissible concentration. (air, water, groundwater and sediment)
A concentration of a substance in the soil, sediment and groundwater at which functions in these compartments will be seriously affected or are threatened to be negatively affected. This is assumed to occur when 50 % of the species and/or 50 % of the microbial and enzymatic processes are possible affected.	SRC eco, Serious Risk Concentration for the ecosystem. (water, soil, groundwater and sediment)	Intervention value* based on SRC eco, (water, soil, groundwater and sediment) if this value is lower than SRC_{human} . SRC_{human} is derived elsewhere.

Derivation of ERLs

ERLs are derived using single-species toxicity data or processes for soil and physico-chemical characteristics, with different approaches depending on the amount of information available. When chronic toxicity data (NOEC = no observed effect concentration) for 4 or more species of at least 4 different taxonomic groups are available for a particular environmental compartment, a statistical procedure is applied to derive ERLs (Aldenberg and Jaworska, 2000). This approach is called refined effect assessment. The basic assumption of the method is that the log of the sensitivities of a set of species in a community can usually be described by a normal distribution. The available ecotoxicological data are seen as a sample from this distribution and are used to estimate the parameters of the species

sensitivity distribution. Specific percentiles of this species sensitivity distribution are chosen to determine ERLs (5th percentile = MPC, 50th percentile = SRCeco)

When fewer data are available a set of assessment factors is applied, varying from 10 to 1000, depending on the type of data. This approach is called the preliminary effect assessment. Assessment factors from the technical guidance document (TGD) of the European Union are used (ECB, 1996). Currently the TGD is being updated and a separate chapter on the effect assessment of substances in marine water will be added. If the base set for using the TGD method is incomplete the modified EPA method is used.

Equilibrium partitioning

If toxicity data for species representative of soil and sediment cannot be found or are insufficient, equilibrium partitioning is applied to derive ERLs for soil and sediment from the ERL for water. In this case soil/water or sediment/water partition coefficients are required. ERL soil and sediment are calculated according to:

1. $ERL (sed/soil) = ERL (water) * K_p$
2. $ERL (sed/soil) = \text{environmental risk limit for terrestrial species using EqP method in } mg\ kg^{-1}$
3. $ERL (water) = \text{environmental risk limit for aquatic species in } mg\ l^{-1}$
4. $K_p = \text{partition coefficient for standard soil or standard sediment.}$

Secondary poisoning

Substances that accumulate through the food chain may exert toxic effects on higher organisms such as birds and mammals. If a substance is potentially bioaccumulative, toxicological data for birds and mammals are collected. Dividing the data by bioaccumulation data (BCF) and using several conversion factors leads to a NOEC water for biota. These NOECs are combined with the available direct toxicity data and the ERLs are calculated according to the methods described above (for details see Traas, 2001).

The added risk approach

For naturally occurring substances, background concentrations (BC) are taken into account. Maximum Permissible Addition (MPA) are calculated using a similar approach as the MPC for substances having no natural background concentration. The MPC is calculated according to the equation:

$$MPC = MPA + BC$$

The negligible concentration is calculated according to:

$$NC = NA + BC, \text{ where } NA = MPA/100$$

Standardisation

ERLs for soil and sediment are calculated for a standardised soil, i.e., for metals a soil or sediment that contains 10% organic matter and 25 % of clay; for organic substances one that contains 10 % organic matter. ERLs for water are reported for dissolved and total concentrations (including a standard amount of suspended matter) and distinguished between freshwater and saltwater if values are significantly different.

References

- Aldenberg, T., and Jaworska, J. 2000. Uncertainty of the hazardous concentration and fraction affected for normal species sensitivity distributions. *Ecotoxicology and environmental safety*, 46: 1–18.
- ECB. 1996. Technical guidance document in support of Commission Directive 93/67/EEC on risk assessment for notified substances and the Commission Regulation (EC) No 1488/94 on risk assessment for existing chemicals. EC Catalogue Numbers CR-48-96-001, 002,003, 004-EN-C. Office for Official Publications of the European Community, 2 Rue Mercier, L-2965 Luxembourg.
- Traas, T.P. 2001. Guidance document on deriving environmental risk limits. RIVM report 601501012.

e) NORWAY

The Norwegian sediment criteria for Classification of Environmental Quality and Degree of Pollution (CEQDP) in fjords and coastal waters represent the basis for assessing environmental quality (see Table A6.8 for values). The EQS is divided into 5 classifications, with the lowest concentration level being based on nationally-derived background values. These background values were developed from surface samples from areas which had no point source contamination, but which were not necessarily free of anthropogenic influence, so that they are not intended to represent pre-industrial values, but rather represent concentrations seen today in uncontaminated areas. There are plans to review the classification.

f) SPAIN

One method for deriving the degree of metal contamination in sediments proposed by Tomlinson *et al.* (1980) follows the approach below. The levels of contamination for metals are estimated from the natural background of metals in the Basque coastline (AZTI, unpublished data) and follow the Müller criteria for sediment classification (Müller, 1979).

$$LPI = (EF_1 \times EF_2 \times EF_3 \dots EF_n)^{1/n}$$

$$EF = C_n/B_n$$

LPI: Load Pollution Index

EF: Enrichment Factor

C_n : metal concentration

B_n : metal background concentration

LPI > 48: extreme contamination (EC)

48 > LPI > 12: strong contamination (SC)

12 > LPI > 3: moderate contamination (C)

3 > LPI > 1: slight contamination (LC)

LPI < 1: no contamination (NC)

The levels of contamination for organic compounds are estimated on the basis of:

- If there are reference values (PCB, DDT, PAH)

NC < detection limit < LC < guide or low toxicity < C < limit or median toxicity < SC

Where NC = non-contaminated, LC = low contamination, C = contaminated, and SC = serious contamination.

- If there are no reference values (HCB, aldrin, dieldrin, t-nonaclor, HCH)

NC < detection limit < LC < 3*detection limit < C < 12*detection limit < SC

In Huelva the sediment quality triad approach is also used in surveillance following the Aznalcollar disaster of 1997.

References

- AZTI. 1998. Borja, A., J. Franco, V. Valencia, A. Uriarte and R. Castro, 1998. Red de vigilancia y control de la calidad de las aguas litorales del País Vasco: otoño 1996-verano 1997. Informe final, para el Departamento de Ordenación del Territorio, Vivienda y Medio Ambiente del Gobierno Vasco. UTE AZTI-LABEIN. Vitoria-Gasteiz, 313 pp. + anexes.
- Muller, G. 1979. Schwermetalle in den Sedimenten des Rheins. Veränderungen seit 1971. Umschau, 79: 78–783.
- Tomlinson, D.L., Wilson, J.G., Marris, C.R., and Jeffrey, D.W. 1980. Problems in the assessment of heavy metal levels in estuaries and the formation of pollution index. Helgolander Meeresuntersuchungen, 33: 566–575.

g) SWEDEN

Introduction

In 1999 the Swedish Environmental Protection Agency established the Swedish Environmental Quality Criteria (EQC) of marine sediments among others (Anon, 1999). The purpose of these criteria is to enable local and regional authorities and others to make accurate assessments of environmental quality on the basis of available data on the state of the environment and thus obtain a better basis for environmental planning and management by objectives. The assessment involves two aspects: one dealing with the appraisal of whether the recorded state has any adverse effects on the environment or our health, the other one with appraisal of the extent to which the recorded state deviates from a “background value”. In most cases the background value represents an estimate of a “natural” state. The results of both appraisals are expressed on a scale of 1–5 (five classes). The criteria on coasts and seas are a tool for determining the environmental quality of the marine environment in terms of three threats to the environment:

- eutrophication;
- toxic organic micro-pollutants and metals;
- physical disturbance (exploitation of the coast).

It is difficult to make a definitive assessment of changes in marine biodiversity at present. The Swedish environmental quality is therefore assessed on the basis of the environmental threats affecting the prospects of preserving biodiversity. The parameters used to assess eutrophication are, among others, nutrients, macrofauna and flora. Metals and toxic organic micro-pollutants are assessed in sediments and organisms. The following text deals with the Swedish criteria in sediments.

Organic micro-pollutants

The Swedish classification is not based on the effects on biota, since at present there is a large gap in knowledge of the effects. Instead the classification of organic micro-pollutants in sediments is based on the statistical distribution of a large data set of the superficial sediments (0–1 cm). This data set comes from the Geological Survey of Sweden, which during the last 15 years has systematically collected sediment samples from the Swedish coast and sea areas and analysed them using the same methods throughout. The classification system for organic contaminants is shown in Table A6.9. These classes have been derived from concentrations found in Swedish waters. Class 1 is set at zero since the organic contaminants do not exist naturally. Further notes on the determination of class boundaries are given with the table.

Metals

The assessment of metals is based on the deviation from a background value representing pre-industrial concentration levels. The background value (Table A6.10) comes from a Normally distributed data set of reference samples collected by the Geological Survey of Sweden in Swedish coastal and sea areas. The reference samples were taken at about 55 cm depth of burial, i.e., where the concentrations are believed to represent those from the pre-industrial period. From the data set, the 50th percentiles have been used as the background values. Natural concentrations of metals in sediments are rather similar along the Swedish coast, although local discrepancies may exist, as for example in the Bothnian Bay off the ore fields. In such cases, a local pre-industrial value may be used as the background value.

Tables A6.11 and A6.12 show the deviation from background values. Table A6.11 shows background values derived from partial digestion (7 M HNO₃) of the sediment following the Swedish standard used in the country since the beginning of the 1970s. Table A6.12 shows background values based on the digestion of the total sediment (HF or LiBO₄-fusion).

One objective of the classification system is that the system should make it possible to detect whether a local point source exists and is affecting a restricted sea area. Thus the boundary between the classes 4 and 5 is put at a level where point sources clearly influence the concentration. Tables A6.13 and A6.14 present the concentration data for the Swedish classification system of sediments. The boundary between class 1 and 2 is set at a ratio of 1, i.e., when the environmental state is equal to the background value, so that the class boundary between classes 1 and 2 should represent a “natural” concentration. The calculated boundaries are based on the background values given in Table A6.10 and the factors given in Tables A6.11 and A6.12. The classes 2, 3 and 4 are intended to successively show the effect of increased diffuse pollution. Table A6.13, using the Swedish standard method, sets the boundary between the classes 4 and 5 at the 95th percentile of a data set from locally unaffected coastal areas (for nickel and chromium the 99th percentile is used). Table A6.14 for total analyses sets the boundary at the 99th percentile of offshore data. Further notes on the determination of class boundaries are given with the tables.

Reference

Anonymous. 1999: Bedömningsgrunder för miljö kvalitet – Kust och hav (Assessments of Environmental Quality – in Coast and sea). Swedish Environmental Protection Agency, Report No. 4914, 134 pp.

h) UNITED KINGDOM

The UK does not currently have any standards for assessment of general environmental quality of sediments. Data collected under the National Marine Monitoring Programme are currently assessed against the available Background/Reference Concentrations as recommended by OSPAR. A review is currently under way to establish a more relevant set of BRC data for the UK.

IIIb DREDGED MATERIAL STANDARDS

Summary

Dredged material disposal is governed by legislation in most countries. The most common approach is a two action level approach, where three concentration classes are defined. Contaminants are measured in a particular size fraction and concentrations compared against limit values in each category:

Category 1: $C < AL$ 1

C = concentration

Category 2: AL 1 < $C < AL$ 2

AL = action level

Category 3: $C > AL$ 2

Concentrations below category 1 (or “target level”) mean that disposal would generally be permitted (subject to consideration of other factors, e.g., volumes, grain size, etc.); those in category 2 indicate moderate contamination and the material would require further study before disposal could be permitted; those in category 3 (“limit” or “intervention” level) represent concentrations so high that disposal at sea would generally not be permitted. Table A6.4 summarises the approaches used in dredged material assessment.

Portugal uses a 5-category system for dredged material assessment, developed from environmental quality standards (Table A6.16). The Netherlands has one overall limit level, above which material may not be disposed of at sea, but also has various sub-levels which are applicable in particular situations (Table A6.17). A few countries operate a “case-by-case” system, where each application for dredge disposal is considered individually and internal guidelines may be applied by the licensing authority (i.e., standards which have no basis in law). In most such instances, the procedure is under review and is likely to be replaced by an action level approach.

Sediment chemistry is the main method by which assessment of the dredged material is made, although some countries are introducing ecotoxicological measures (e.g., Belgium, Germany).

Table A6.4. Summary of approaches used for dredged material assessment

Country	General approaches used	No. of categories in action level approach	Methods used in development of action levels	Notes
Belgium	Action level	3	1) sediment chemistry 2) bioassays	Quality criteria based on mean contaminant concentration in marine navigation channels
Denmark	Action level (see notes)	3	sediment chemistry	Not yet implemented in law
Finland	Case-by-case	---	---	Legislation for sediment quality criteria in preparation
France	Action level	3	sediment chemistry	
Germany	Action level	3	1) sediment chemistry 2) bioassays	
Portugal	Action level and case-by-case	5	sediment chemistry	Physical, biochemical, biological, toxicological and persistence properties of the dredged material are analysed in a case-by-case approach
Netherlands	Action level	1 limit level#	sediment chemistry	Biological effects methods being tested. #Sub-levels for particular situations depending upon use
Norway	Action level + case-by-case	5	sediment chemistry	Categorisation is the same as used for environmental quality standards
Ireland	Case-by-case: Action levels under development	---	---	3 category action level approach under development
Spain	Action level	3	sediment chemistry	Sediment chemistry not yet implemented in law. Sediment bioassays under development
Sweden	?			
UK	England and Wales (E+W): Case-by-case approach: Action levels to be implemented shortly.	---		E+W: 3-category action level approach in preparation. Scotland: Data assessed against OSPAR BRCs

Comparison of standards for assessment of dredged material disposal at sea

Table A6.5 summarises the range of contaminant concentrations used in the assessment of dredged material, while Tables A6.15–A6.19 report the details of these values.

For most substances considered, there is some consistency among the concentrations set for target concentration values. Ranges in limit values are much higher however, and this cannot generally be explained by differences in grain size. It seems more likely that the large differences between limit values in different countries instead reflect local conditions.

Table A6.5. Summary of concentration ranges used in the assessment of dredged material for disposal at sea.

Contaminant	Units	TARGET VALUES			LIMIT VALUES		
		Range	Class range ¹ (Portugal)	Max value in <2 mm fraction ²	Range	Class range ¹ (Portugal)	Max value in <2 mm fraction ²
As	mg/kg	20–80	2	*	50–1000	3 –	*
Cd	mg/kg	0.5–2.5	2	*	2.4–12.5	2–4	7
Cr	mg/kg	60–300	2–3	*	180–5000	3–4	1000
Cu	mg/kg	20–150	2	*	90–1500	2–4	400
Hg	mg/kg	0.1–1	1–2	0.6	0.8–5	2–4	*
Ni	mg/kg	37–130	2–3	*	45–1500	2–5	*
Pb	mg/kg	30–120	1–2	*	100–1500	2–5	*
Zn	mg/kg	160–700	1–3	*	500–10000	2–5	*
sum7 PCB	µg/kg	2–500	2–3	*	2–1000	1–4	*
PCB - 28	µg/kg	1–25	*	*	6–50	*	*
PCB - 52	µg/kg	1–25	*	*	3–50	*	*
PCB - 101	µg/kg	2–50	*	*	6–100	*	*
PCB - 118	µg/kg	3–25	*	*	10–50	*	*
PCB - 138	µg/kg	4–50	*	*	12–100	*	*
PCB - 153	µg/kg	4–50	*	*	15–100	*	*
PCB - 180	µg/kg	2–25	*	*	6–50	*	*

Notes

1) Portugal uses a class range system for assessment of dredge material: numbers in this column show over which classes the target or limit range values fall.

2) Where maximum concentration range was in the fine fraction (<20 µm), maximum concentration in the <2 mm is given in this column.

A summary of the preparation and digestion or extraction methods for assessment of dredged material used by member countries is given in Table A6.16. Most countries analyse the <2 mm fraction; Belgium and Spain examine the <63 µm fraction and Germany the <20 µm. Analysis of metals is done after digestion by HF (total) or HNO₃ (partial). It may thus be difficult to directly compare action level values when differing techniques are applied. Likewise for organic contaminants different results can be found when soft extractions like Acetone-SPE, or extractions under harsh conditions using ASE or saponification, are applied.

Further notes to Table A6.5.

A 3-category approach is assumed unless stated below. Tables A6.15–A6.18 show actual concentration data for sediment quality criteria.

BELGIUM

Dredged material to be dumped at sea must satisfy the criteria shown in Table A6.15. If analysis results exceed the limit for three of the criteria, the dredged material may not be dumped at sea. If a concentration falls between the target value and the limit value, the number of sample analyses is increased. If concentrations are still in this zone then bioassays will be undertaken. <http://www.mumm.ac.be/EN/Management/Sea-based/dredging.php>.

DENMARK

Denmark is currently developing its system for licensing disposal at sea, and the planned approach is to use locally derived background concentrations. The current view of the EPA is to develop a 3-category system according to the following limits. The proposed approach to management of dredged material disposal is as follows:

Decision	Metals	Organics
Disposal at sea permitted	$\leq 2 \times \text{background}$	$\leq 2 \times \text{background}$
Disposal subject to conditions	$\leq 2 \times \text{background}$	$40\text{--}100 \times \text{background}$
Disposal at sea not permitted	$> 2 \times \text{background}$	$>40 \times \text{--} >100 \times \text{background}$

For TBT, the EPA may allow sea disposal on the basis of total amount of substance above the “background” level, if the total amount of TBT to be disposed is less than 1 kg and no acute effects are expected.

Under application of the new regulations, the contaminants which will cause the most problems for dredging applications are TBT>PAH>Cu and Hg.

FINLAND

A case-by-case system is used for permits for disposal of dredged material at sea. A project is currently examining sediment quality criteria for dredged material although implementation dates are not yet fixed. The proposed criteria have been set according to the following principles:

For metals, Level 1 is usually set at $1.5 \times$ average of background values; ($2.5 \times$ for mercury), while Level 2 is based on the highest allowable level of toxicity (Maximum Acceptable Risk Level = MAR) or on the Canadian toxicity threshold level (TEL).

For PCB and DDT, Levels 1 and 2 are set the same as those in the Netherlands. Only the *p,p'* forms of DDT and its derivatives are considered; when measuring accuracy is 0.01 mg/kg, only threefold concentrations and higher are counted.

For mineral oils, Levels 1 and 2 are set as in the Netherlands from the PAH MAR concentrations. For PAH compounds, Level 1 = MAR/100; Level 2 < MAR. For dioxins and furans the limit values are taken from the proposal of the National Health Institute, where toxicity is calculated according to the newest WHO TEF values for mammals.

Reference

<http://www.who.int/pcs/docs/dioxin-exec-sum/exe-sum-final.html>

Van den Berg, M., Birnbaum, L., Bosveld, B.T.C., Brunström, B., Cook, P., Feeley, M., Giesy, J.P., Hanberg, A., Hasegawa, R., Kennedy, S.W., Kubiak, T., Larsen, J.C., van Leeuwen, F.X.R., Liem, A.K.D., Nolt, C., Peterson, R.E., Poellinger, L., Safe, S., Schrenk, D., Tillitt, D., Tysklind, M., Younes, M., Waern, F., and Zacharewski, T. 1998. Toxic Equivalency Factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environmental Health Perspective*, 106 (12): 775–792.

GERMANY

Germany established action levels for the chemical and biological assessment of dredged material from the German federal waterways. Currently, these action levels do not apply to waters under the responsibility of the Federal States (Länder). However, they are currently under review with the aim to extend their applicability to all German waterways. Dredge disposal quality criteria are derived from presently prevailing contaminant concentrations in the North Sea Wadden Sea sediments from 1982–1987. A 3-category approach is used for disposal at sea:

Action Level 1: reference value derived from locally derived sediments (Wadden Sea);

Action Level 2: five times the reference value for metals and three times for organic contaminants.

The action levels represent management values and are neither ecotoxicological quality criteria nor quality targets (Table A6.15). Action levels for organotin compounds are still under discussion.

In order to describe the toxicologically effective pollution load of sediments and dredged materials, an evaluation method for the toxicological investigations of pore water, sediment elutriates and extracts was developed (Krebs, 1988, 1999). These phases should be examined with standardized tests of aquatic toxicity, using dilution series in geometric

sequence with a dilution factor of two. The toxicological evaluation is then simplified to identify the first dilution step that is no longer toxic.

For the numerical designation of the toxicity the first non-toxic dilution factor is used. The pT-value (potentia toxicologiae = toxicological exponent) is the exponent of toxicity and is defined as the negative binary logarithm of the first non-toxic dilution factor in a dilution series in geometric sequence with a dilution factor of two. Accordingly, the pT-value gives an indication of how many times a sample must be diluted in the ratio 1:2 to reach a stage of no toxic effect.

The pT-value of the most sensitive organism within a test battery determines the toxicity class of the dredged material. Different bioassays and different test phases (e.g., pore water, elutriate) are considered equal in rank. The toxicity classes are assigned Roman numerals. If the highest pT-value is 5, for instance, then the tested material is assigned to toxicity class V. The highest level of this classification of dredged material is toxicity class VI, which includes pT-values from 6 to ∞ . Regarding the handling of dredged material, the toxicity classes defined by the pT-value method are assigned to the categories “unproblematic” (toxicity classes 0, I, II), “moderately critical” (toxicity classes III and IV), and “highly critical” (V and VI) (Table A6.19).

References

- Krebs, F. 1988. Der pT-Wert: Ein gewässerökotoxikologischer Klassifizierungsmaßstab (The pT-value: An aquatic ecotoxicological classification index).- GIT-Fachzeitschrift für das Laboratorium, 32: 293–296.
- Krebs, F. 1999. Ökotoxikologische Klassifizierung von Sedimenten mit Hilfe der pT-Wert-Methode (Ecotoxicological classification of sediments with the pT-value method).- In U. Kern und B. Westrich (Hrsg.): Methoden zur Erkundung, Untersuchung und Bewertung von Sedimentablagerungen und Schwebstoffen in Gewässern (Exploration, investigation and assessment of sediment deposits and suspended particulate matter in aquatic systems). Schriftenreihe des Deutschen Verbandes für Wasserwirtschaft und Kulturbau e.V. (DVWK). Heft, 128: 297–303.

ITALY

Legislation involves a number of decrees which have been issued over the last 20 years. The sea disposal of dredged material which can be classified as toxic/noxious is not allowed under Italian legislation (DECRETO 24 gennaio 1996).

THE NETHERLANDS

A maximum concentration limit is set for material for dredge disposal at sea (Table A6.18). There are also lower limits for particular uses of water bodies. A higher limit is set for metals which are known to be in anaerobic sediments, since these will be bound as sulphides.

NORWAY

Dredging activities are of minor importance in Norway (few hundred thousand tonnes annually), and data are currently assessed against the environmental quality standards (Classification of Environmental Quality and Degree of Pollution (CEQDP) in fjords and coastal waters). A case-by-case basis for assessment of dredged material is performed. Certain analytes must be measured in material proposed for dredge disposal, while others may be required by the authority according to local conditions. The overall authority is the State Pollution Control Authority, but disposal permits may also be granted by county authorities.

PORTUGAL

Legislation is used to regulate dredged material disposal (DR II n° 141 21/6/1995). The quality criteria standard regulations define the method for disposal of the dredged material. A 5-category approach is used to classify material for disposal (Table A6.17) as follows:

Class 1: may be disposed of in the aquatic medium or at places exposed to erosion or used to feed beaches without restrictions.

Class 2: may be disposed of in the aquatic medium subjected to the characteristics of the receiving medium and its legitimate use.

Class 3: may be disposed of on land to reclaim an area to the sea and if to be disposed at sea, requires adequate study of the disposal place and post-monitoring.

Class 4: to be disposed of on land in a prepared place, including soil impermeability measures and with a recommendation for the spoil to be covered with impermeable soil.

Class 5: should not be dredged. If dredging is absolutely necessary the dredged material must be treated as industrial waste (specific law being applied). It is forbidden to be disposed of in water or on land.

REPUBLIC OF IRELAND

Figure A6.1 summarises the Republic of Ireland's existing procedures towards dredged material assessment. To date, the sediment chemistry of dredged material in Ireland has been considered on a case-by-case basis, using provisional action levels. These are guideline figures for the assessment of the sediment and it is intended to derive final action levels for sediment chemistry. These will be built around the background quality of Irish sediments, taking into account the experiences of other countries.

If the volume of sediment is below a provisional figure of 10,000 m³, and material is thought to be unaffected by local sources of contamination or is composed entirely of material greater than 2 mm particle size (gravel and larger), then further testing may not be required. This may also be the case for material dredged from capital projects. Material consisting largely of sand is unlikely to be contaminated (apart from flakes of TBT) and a permit may be granted without further testing, providing no known source of TBT exists in the vicinity.

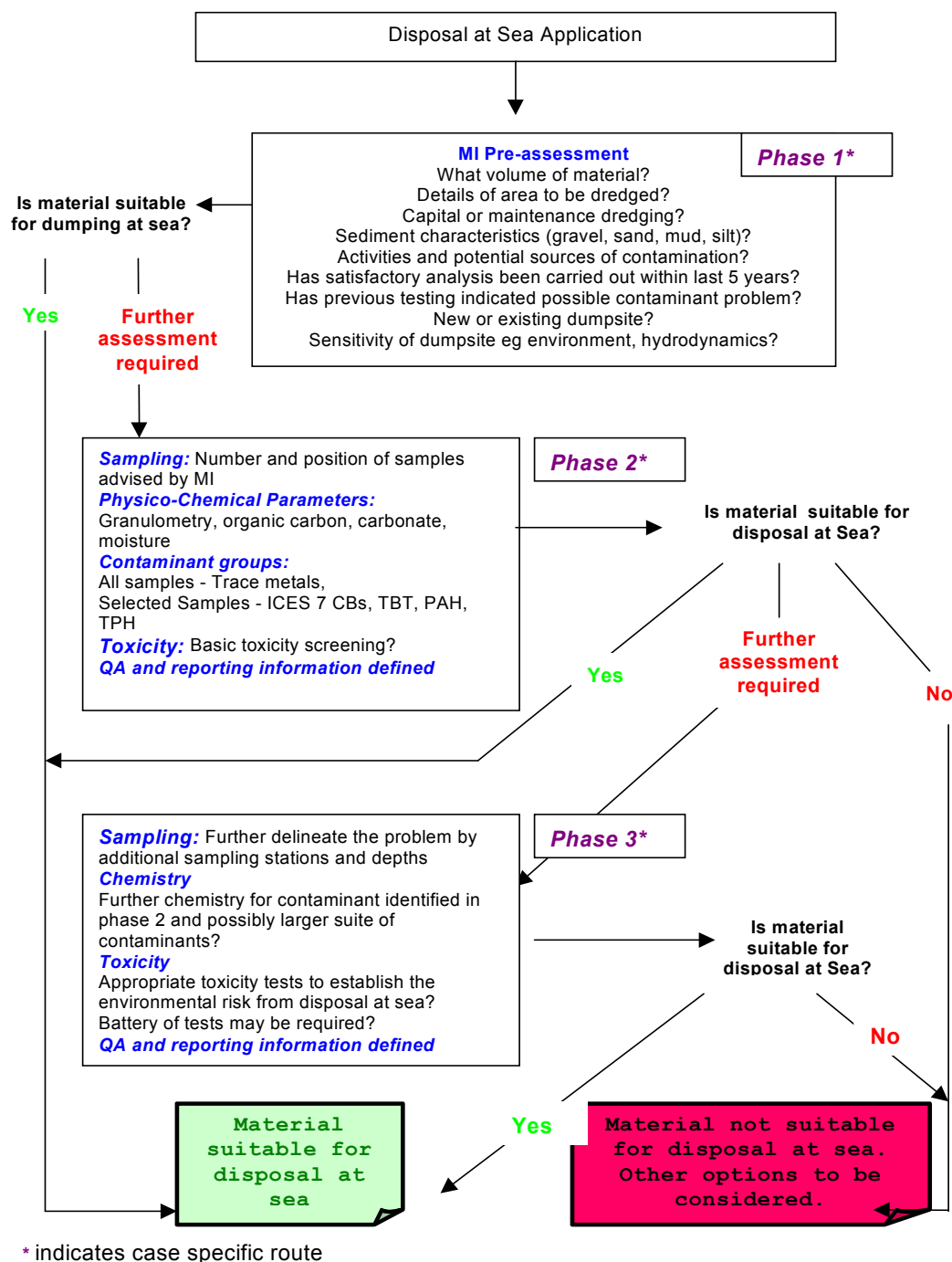


Figure A6.1. Assessment of sediments with respect to chemical contamination for disposal at sea permission in the Republic of Ireland (with permission from Margot Cronin and Evin McGovern, Marine Institute).

SPAIN

The Spanish recommendations were published by CEDEX in 1994 and are currently under revision. They are expected to be legally implemented towards the end of 2004. Standards apply to fine sediments (<63 µm) with more than 10 % of fine material and to those with more than 10 % of organic matter using a 3-category approach. Sediments with metal concentrations above the second level and = 8 × Level 2, have to be isolated and belong to category IIIa. Sediments with metal concentrations higher than 8 × level 2, must be isolated into containers or into a contained area (category IIIb). Locally-derived background concentrations are under development.

Bioassays under development for application to dredged material assessment are *Microtox*, *Ampelisca* or *Corophium* and a crustacean.

UNITED KINGDOM

England and Wales, Scotland, and Northern Ireland have separate but equivalent bodies that implement marine disposal of dredged material. A case-by-case approach is adopted throughout the UK, although England and Wales are currently developing an action level approach towards the assessment of dredged material. Dredging disposal to sea is governed by Part II of the Food and Environmental Protection Act 1985 (FEPA). Assessments of the impacts are based on:

- the material to be disposed (physico-chemical analysis);
- method of dredging and disposal;
- disposal site characteristics;
- other disposal options, especially beneficial uses.

The basis for setting standards was suggested in two Environmental Quality objectives relevant to sediments (MAFF, 1989):

1 General ecosystem conservation.

Objective: Maintenance of environmental quality so as to protect aquatic life and dependent non-aquatic organisms, such that the ecosystem is typical of coastal water with those physical characteristics and latitude. Basis of standard: Grain-size, carbon/nitrogen and toxic substances to be below levels of effect, and within any EQS set by relevant legislation.

2 Preservation of the natural environment.

Objective: Outwith the immediate disposal zone, the quality of the receiving environment will be indistinguishable from that of the adjacent estuarine or marine environment. Basis of standard: Minimal percentage change over background levels of metals and other contaminants. No continuing upward trends after “steady-state” is achieved.

Action levels currently being derived for England and Wales have been set according to the following approach. Action Level 1 is set at an estimate of the median background concentration, i.e., based on sediment chemistry. Action level 2 is guided by the ERM and TEL values produced by Long *et al.* (1995; 1998; 1998). It is expected that experience in the use of the values, and collection of data applicable to the local situation, will allow revision of the Action Levels in a few years' time.

References

- Long, E., MacDonald, D., Smith, S., and Calder, F. 1995. 'Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments.' *Environmental Management*, **19**(1): 81–97.
- Long, E., Field, J., and MacDonald, D. 1998. Predicting toxicity in marine sediments with numerical sediment quality guidelines. *Environ Toxicol Chem*, **17**(4): 714–727.
- Long, E., and MacDonald, D. 1998. Recommended uses of empirically derived, sediment quality guidelines for marine and estuarine ecosystems. *Human Ecol Risk Assess*, **4**(5): 1019–1039.
- MAFF. 1989. First Report of the Marine Pollution Monitoring Management Group's Coordinating Group on Monitoring of Sewage-sludge Disposal Sites. *Aquat. Environ. Monit. Rep.*, MAFF Direct. Fish. Res., Lowestoft, 20, 64 pp.

TABLES A6.6-A6.14 ENVIRONMENTAL QUALITY STANDARDS FOR SEDIMENTS

Table A6.6. Canadian sediment quality guidelines for the protection of aquatic life. Interim marine sediment quality guidelines (ISQGs; dry weight), probable effects levels (PELs; dry weight) and incidence (%) of adverse biological effects in concentration ranges defined by these values.

Substance	units	ISQG	PEL	% ≤ ISQG	ISQG < %PEL	% ≥ PEL
As	mg kg ⁻¹	7.24	41.6	3	13	47
Cd	mg kg ⁻¹	0.7	4.2	6	20	71
Cr	mg kg ⁻¹	2.26	4.79	9	12	17
Cu	mg kg ⁻¹	18.7	108	9	22	56
Hg	mg kg ⁻¹	0.13	0.7	8	24	37
Pb	mg kg ⁻¹	30.2	112	6	26	58
Zn	mg kg ⁻¹	124	271	4	27	65
DDT ¹	µg kg ⁻¹	1.19	4.77	8	5	59
DDD ¹	µg kg ⁻¹	1.22	7.81	4	11	46
DDE ¹	µg kg ⁻¹	2.07	374	5	16	50
Dieldrin	µg kg ⁻¹	0.71	4.3	4	13	50
total PCBs	µg kg ⁻¹	21.5	189	16	37	55
PCDDs and PCDFs	ng TEQ kg ⁻¹	0.85	21.5	*	*	*
Acenaphthene	µg kg ⁻¹	6.71	88.9	8	29	57
Acenaphthylene	µg kg ⁻¹	5.87	128	7	14	51
Anthracene	µg kg ⁻¹	46.9	245	9	20	75
Benz[<i>a</i>]anthracene	µg kg ⁻¹	74.8	693	9	16	78
Benzo[<i>a</i>]pyrene	µg kg ⁻¹	88.8	763	8	22	71
Chrysene	µg kg ⁻¹	108	846	9	19	72
Dibenz[<i>a,h</i>]anthracene	µg kg ⁻¹	6.22	135	16	12	65
Fluoranthene	µg kg ⁻¹	113	1494	10	20	80
Fluorene	µg kg ⁻¹	21.2	144	12	20	70
2-Methylnaphthalene	µg kg ⁻¹	20.2	201	0	23	82
Naphthalene	µg kg ⁻¹	34.6	391	3	19	71
Phenanthrene	µg kg ⁻¹	86.7	544	8	23	78
Pyrene	µg kg ⁻¹	153	1398	7	19	83

Notes

1) sum of *p,p'* and *o,p'* isomers

Table A6.7. Environmental quality classifications for sediment in The Netherlands. All values dry weight sediment. Values normalised to sediment content 5% TOC, 10% clay for metals and 5% organic carbon for organic contaminants.

		Long-term	Short-term
Contaminant	Unit	NC	MPC
Cd	mg kg ⁻¹	0.8	12
Inorganic Hg	mg kg ⁻¹	0.3	10
Organic Hg	mg kg ⁻¹	0.3	1.4
Cu	mg kg ⁻¹	36	73
Ni	mg kg ⁻¹	35	44
Pb	mg kg ⁻¹	85	530
Zn	mg kg ⁻¹	140	520
Cr	mg kg ⁻¹	100	380
As	mg kg ⁻¹	29	55
Naphthalene	µg kg ⁻¹	1	100
Anthracene	ug kg ⁻¹	1	100
Phenanthrene	µg kg ⁻¹	5	500
Fluoranthene	µg kg ⁻¹	30	3000
Benz[a]anthracene	µg kg ⁻¹	3	400
Chrysene	µg kg ⁻¹	100	11000
Benzo[k]fluoranthene	µg kg ⁻¹	20	2000
Benzo[a]pyrene	µg kg ⁻¹	3	3000
Benzo[ghi]perylene	µg kg ⁻¹	80	8000
Indeno[123cd]Pyrene	µg kg ⁻¹	60	6000
Pentachlorobenzene	µg kg ⁻¹	1	100
Hexachlorobenzene	µg kg ⁻¹	0.05	5
Pentachlorophenol	µg kg ⁻¹	2	300
Aldrin	µg kg ⁻¹	0.06	6
Dieldrin	µg kg ⁻¹	0.5	450
Endrin	µg kg ⁻¹	0.04	4
DDT	µg kg ⁻¹	0.09	9
DDD	µg kg ⁻¹	0.02	2
DDE	µg kg ⁻¹	0.01	1
α -Endosulfan	µg kg ⁻¹	0.01	1
α-HCH	µg kg ⁻¹	3	290
β -HCH	µg kg ⁻¹	9	920
c-HCH	µg kg ⁻¹	0.05	230
Heptachlor	µg kg ⁻¹	0.7	0.7
Heptachlorepoxyde	µg kg ⁻¹	0.0002	0.02
Chlordane	µg kg ⁻¹	0.03	3
Total Hydrocarbons	µg kg ⁻¹	50	1000
PCB-28	µg kg ⁻¹	1	4
PCB-52	µg kg ⁻¹	1	4
PCB-101	µg kg ⁻¹	4	4
PCB-118	µg kg ⁻¹	4	4
PCB-138	µg kg ⁻¹	4	4
PCB-153	µg kg ⁻¹	4	4
PCB-180	µg kg ⁻¹	4	4

Table A6.8. Environmental quality classifications for sediment in Norway. < 2mm fraction, dry weight.

Contaminant	Units	Class 1 (Good)	Class 2 (Fair)	Class 3 (Poor)	Class 4 (Bad)	Class 5 (Very bad)
Ag	mg kg ⁻¹	<0.3	0–1.3	1–5	5–10	>10
As	mg kg ⁻¹	<20	20–80	80–400	400–1000	>1000
Cd	mg kg ⁻¹	<0.25	0.25–1	1–5	5–10	>10
Cr	mg kg ⁻¹	<70	70–300	300–1500	1500–5000	>5000
Cu	mg kg ⁻¹	<35	35–150	150–700	700–1500	>1500
F	mg kg ⁻¹	<800	800–3000	3000–8000	8000–20000	>20000
Hg	mg kg ⁻¹	<0.15	0.15–0.6	0–3	3–5	>5
Pb	mg kg ⁻¹	<30	30–120	120–600	600–1500	>1500
Ni	mg kg ⁻¹	<30	30–130	130–600	600–1500	>1500
Zn	mg kg ⁻¹	<150	150–650	650–3000	3000–10000	>10000
TBT ¹	µg kg ⁻¹	<1	5	5–20	20–100	>100
Sum PAHs ²	µg kg ⁻¹	<300	300–2000	2000–6000	6000–20000	>20000
Sum 7 PCB ³	µg kg ⁻¹	<5	5–25	25–100	100–300	>300
B(a)P	µg kg ⁻¹	<10	10–50	50–200	200–500	>500
EPOCl ⁴	µg kg ⁻¹	<100	100–500	500–2000	2000–15000	>15000
TE _{PCDF/D} ⁵	µg kg ⁻¹	<0.01	0.01–0.03	0.03–0.10	0.10–0.5	>0.5
Sum DDT ⁶	µg kg ⁻¹	<0.5	0.5–2.5	2.5–10	10–50	>50
Hexachlorobenzene	µg kg ⁻¹	<0.5	0.5–2.5	2.5–10	10–50	>50

Notes

- 1) TBT: Tributyltin as the molecule
- 2) PAH: Polycyclic aromatic hydrocarbons, sum PAHs: sum of tri- to hexacyclic compounds including the 16 in EPA protocol 8310. The dicyclic naphthalenes are not included. The sum also includes all potentially carcinogen PAHs (group 2A and 2B in IARC, 1987).
- 3) PCB: Polychlorinated biphenyls, sum PCB-7: total of congeners (CB) 28, 52, 101, 118, 138, 153, 180.
- 4) EPOCl: Extractable persistent organically bound chlorine.
- 5) TE_{PCDF/D}: Toxic Equivalents of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (dioxins). Within PCDF/PCDD there is a small group of very toxic compounds. These can be expressed as toxic-equivalents (TE) of the most toxic compound (2,3,7,8-TCDD).
- 6) DDT: Diphenyltrichloroethylene: sum DDT is the total of DDT and metabolites DDE and DDD.

Table A6.9 Swedish Environmental Criteria for organic micro-pollutants in coast and sea sediments Measured in the <2 mm fraction and expressed in ug kg⁻¹ dry matter.

Substance	Class I "None"	Class II "Low concentration"	Class III "Moderate concentration"	Class IV "High concentration"	Class V "Very high concentration"
Phenanthrene	0	0 – 10	10 – 30	30 – 100	> 100
Anthracene	0	0 – 2	2 – 8	8 – 30	> 30
Fluoranthene	0	0 – 20	20 – 80	80 – 270	> 270
Pyrene	0	0 – 12	12 – 50	50 – 200	> 200
Benzo[<i>a</i>]anthracene	0	0 – 10	10 – 35	35 – 110	> 110
Chrysene	0	0 – 13	13 – 50	50 – 180	> 180
Benzo[<i>b</i>]fluoranthene	0	0 – 50	50 – 150	150 – 400	> 400
Benzo[<i>k</i>]fluoranthene	0	0 – 20	20 – 50	50 – 160	> 160
Benzo[<i>a</i>]pyrene	0	0 – 20	20 – 60	60 – 180	> 180
Benzo[<i>ghi</i>]perylene	0	0 – 30	30 – 100	100 – 350	> 350
Indeno[<i>cd</i>]pyrene	0	0 – 50	50 – 170	170 – 600	> 600
sum 11 PAHs	0	0 – 280	280 – 800	800 – 2,500	> 2,500
HCB	0	0 – 0.04	0.04 – 0.2	0.2 – 1	> 1
PCB 28	0	0 – 0.06	0.06 – 0.2	0.2 – 0.6	> 0.6
PCB 52	0	0 – 0.06	0.06 – 0.2	0.2 – 0.8	> 0.8
PCB 101	0	0 – 0.16	0.16 – 0.6	0.6 – 2	> 2
PCB 118	0	0 – 0.15	0.15 – 0.6	0.6 – 2	> 2
PCB 153	0	0 – 0.03	0.03 – 0.3	0.3 – 3.5	> 3.5
PCB 138	0	0 – 0.3	0.3 – 1.2	1.2 – 4.1	> 4.1
PCB 180	0	0 – 0.1	0.1 – 0.4	0.4 – 1.9	> 1.9
sum 7 PCB (Dutch)	0	0 – 1.3	1.3 – 4	4 – 15	> 15
Total PCB	0	0 – 5	5 – 20	20 – 75	> 75
α-HCH	0	0 – 0.01	0.01 – 0.07	0.07 – 0.3	> 0.3
β-HCH	0	0 – 0.03	0.03 – 0.3	0.3 – 3	> 3
γ-HCH	0	0 – 0.01	0.01 – 0.1	0.1 – 1.3	> 1.3
sum HCH	0	0 – 0.03	0.03 – 0.3	0.3 – 3	> 3
γ-chlordane	0	0 – 0.01	0.01 – 0.04	0.04 – 0.1	> 0.1
α-chlordane	0	0 – 0.02	0.02 – 0.04	0.04 – 0.1	> 0.1
<i>Trans</i> -nonachlor	0	0 – 0.02	0.02 – 0.05	0.05 – 0.15	> 0.15
sum chlordanes	0	0 – 0.02	0.02 – 0.08	0.08 – 0.3	> 0.3
<i>p,p'</i> -DDT	0	0 – 0.02	0.02 – 0.1	0.1 – 0.7	> 0.7
<i>p,p'</i> -DDE	0	0 – 0.2	0.2 – 0.7	0.7 – 2.5	> 2.5
<i>p,p'</i> -DDD	0	0 – 0.13	0.13 – 0.8	0.8 – 5	> 5
sum DDT	0	0 – 0.2	0.2 – 1	1 – 6	> 6
EOCl	0	0 – 600	600 – 4,000	4,000 – 30,000	> 30,000
EOBr	0	0 – 400	400 – 1,000	1,000 – 3,000	> 3,000
EPOCl	0	0 – 150	150 – 700	700 – 3,000	> 3,000
EPOBr	0	0 – 90	90 – 250	250 – 800	> 800

Notes to Table A6.9.

EOCl = Total extractable organic chlorine; EPOCl = Total persistent extractable organic chlorine;

EOBr = Total extractable organic bromine; EPOBr = Total persistent extractable organic bromine.

Class 1 is set at zero as these contaminants do not occur naturally. The boundary between classes 2 and 3 is at the 5th percentile of the data set, corresponding to samples not affected by point sources. That between classes 3 and 4 was determined from the 5th percentile multiplied by the square root of the ratio between the 5th and 95th percentiles. The 95th percentile has been used for the boundary between classes 4 and 5, except in the case of EOCl (90th percentile).

Table A6.10. Background values for metals in sediment (mg kg⁻¹ dry weight) used in the Swedish classification system of Environmental Quality Criteria.

Method	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn
Partial digestion (7 M HNO ₃)	10	0.2	12	40	15	0.04	30	25	85
Total digestion	10	0.2	14	80	15	0.04	33	31	85

Table A6.11. The classification factors of the deviation in the surficial sediment (0–2 cm) from the background value, based on partial digestion of the sediment (leaching at 7 M HNO₃).

Metal Partial digestion (7 M HNO ₃).	Class I “No/very small deviation”	Class II “Small deviation”	Class III “Clear deviation”	Class IV “Large deviation”	Class V “Very large deviation”
Arsenic	≤ 1.0	1.0 – 1.7	1.7 – 2.8	2.8 – 4.5	> 4.5
Cadmium	≤ 1.0	1.0 – 2.5	2.5 – 6.0	6.0 – 15	> 15
Cobalt	≤ 1.0	1.0 – 1.7	1.7 – 2.9	2.9 – 5.0	> 5.0
Chromium	≤ 1.0	1.0 – 1.2	1.2 – 1.5	1.5 – 1.8	> 1.8
Copper	≤ 1.0	1.0 – 2.0	2.0 – 3.3	3.3 – 5.3	> 5.3
Mercury	≤ 1.0	1.0 – 3.0	3.0 – 10	10 – 25	> 25
Nickel	≤ 1.0	1.0 – 1.5	1.5 – 2.2	2.2 – 3.3	> 3.3
Lead	≤ 1.0	1.0 – 1.6	1.6 – 2.6	2.6 – 4.4	> 4.4
Zinc	≤ 1.0	1.0 – 1.5	1.5 – 2.4	2.4 – 4.2	> 4.2

Table A6.12. The classification factors of the deviation in the surficial sediment (0–2 cm) from the background value based on total digestion of the sediment.

Metal Total digestion	Class I “No/very small deviation”	Class II “Small deviation”	Class III “Clear deviation”	Class IV “Large deviation”	Class V “Very large deviation”
Arsenic	≤ 1.0	1.0 – 1.6	1.6 – 2.6	2.6 – 4.0	> 4.0
Cadmium	≤ 1.0	1.0 – 2.5	2.5 – 6.0	6.0 – 15	> 15
Cobalt	≤ 1.0	1.0 – 1.4	1.4 – 2.0	2.0 – 2.8	> 2.8
Chromium	≤ 1.0	1.0 – 1.4	1.4 – 2.0	2.0 – 2.8	> 2.8
Copper	≤ 1.0	1.0 – 2.0	2.0 – 4.0	4.0 – 8.0	> 8.0
Mercury	≤ 1.0	1.0 – 2.6	2.6 – 6.8	6.8 – 18	> 18
Nickel	≤ 1.0	1.0 – 1.3	1.3 – 1.7	1.7 – 2.4	> 2.4
Lead	≤ 1.0	1.0 – 1.5	1.5 – 2.2	2.2 – 3.3	> 3.3
Zinc	≤ 1.0	1.0 – 1.5	1.5 – 2.3	2.3 – 3.5	> 3.5

Table A6.13. The actual concentration boundaries of the Swedish classification system of superficial sediment (0–2 cm), based on partial digestion of the sediment. The values have been calculated by using the background value (Table A6.10) and the factors in Table A6.11.

Metal Partial digestion (7 M HNO₃).	Class I “No/very small deviation”	Class II “Small Deviation”	Class III “Clear deviation”	Class IV “Large deviation”	Class V ”Very large deviation”
Arsenic	≤ 10	10 – 17	17 – 28	28 – 45	> 45
Cadmium	≤ 0.2	0.2 – 0.5	0.5 – 1.2	1.2 – 3	> 3
Cobalt	≤ 12	12 – 20	20 – 35	35 – 60	> 60
Chromium	≤ 40	40 – 48	48 – 60	60 – 72	> 72
Copper	≤ 15	15 – 30	30 – 50	50 – 80	> 80
Mercury	≤ 0.04	0.04 – 0.12	0.12 – 0.4	0.4 – 1.0	> 1.0
Nickel	≤ 30	30 – 45	45 – 66	66 – 99	> 99
Lead	≤ 25	25 – 40	40 – 65	65 – 110	> 110
Zinc	≤ 85	85 – 128	128 – 204	204 – 357	> 357

Table A6.14. The actual concentration boundaries of the Swedish classification system of superficial sediment (0–2 cm), based on **total digestion** of the sediment. The values have been calculated by using the background value (Table A6.10) and the factors in Table A6.12.

Metal Total digestion	CLASS I “No/Very small deviation”	Class II “Small deviation”	Class III “Clear deviation”	Class IV “Large deviation”	Class V ”Very large deviation”
Arsenic	≤ 10	10 – 16	16 – 26	26 – 40	> 40
Cadmium	≤ 0.2	0.2 – 0.5	0.5 – 1.2	1.2 – 3	> 3
Cobalt	≤ 14	14 – 20	20 – 28	28 – 40	> 40
Chromium	≤ 80	80 – 112	112 – 160	160 – 224	> 224
Copper	≤ 15	15 – 30	30 – 60	60 – 120	> 120
Mercury	≤ 0.04	0.04 – 0.1	0.1 – 0.27	0.27 – 0.72	> 0.72
Nickel	≤ 33	33 – 43	43 – 56	56 – 79	> 79
Lead	≤ 31	31 – 47	47 – 68	68 – 102	> 102
Zinc	≤ 85	85 – 128	128 – 196	196 – 298	> 298

Notes to Tables A6.13 and A6.14:

Class 1 is derived from the background value (Table A6.10). The other class boundaries have been defined statistically by multiplying each value of the boundary with a factor. This factor is defined as the cubic root of the ratio between the boundary between classes 4 and 5 and the background value. The boundary between the classes 2 and 3 is found when multiplying the factor with the background value. The boundary between the classes 3 and 4 is calculated from the value of the class boundary by multiplying this value with the factor. That between classes 4 and 5 is given by the 95th percentile of the partial digestion result and the 99th percentile for the total digestion. Class 5 is further divided into three subclasses focused on finding contaminated “hot spots” that have to be treated in one or the other way to diminish the health risk.

TABLES A6.15–A6.19 STANDARDS FOR DREDGED MATERIAL DISPOSAL AT SEA

Table A6.15. Action levels for dredged material disposal assessment, data based on dry weight.

		Belgium		Finland PROPOSED 25% clay 10% organics		France		Germany		Norway		Spain		Sweden		United Kingdom England+Wales ¹ < 63 µm Action levels being derived		
	Grain Size/ sediment composition	< 2 mm				< 2 mm		< 20 µm		< 2 mm		< 63 µm >10% fine fraction and >10% organic matter		< 2 mm				
Contaminant	Action level	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	
As	mg kg ⁻¹	20	100	15	60	25	50	30	150	80	1000	80	200	30	100			
Cd	mg kg ⁻¹	2.5	7	0.5	2.5	1.2	2.4	2.5	12.5	1	10	1	5	0.9	3			
Cr	mg kg ⁻¹	60	220	65	270	90	180	150	750	300	5000	200	1000	60	200			
Cu	mg kg ⁻¹	20	100	50	90	45	90	40	200	150	1500	100	400	60	200			
Hg	mg kg ⁻¹	0.3	1.5	0.1	1	0.4	0.8	1	5	0.6	5	0.6	3	0.3	1			
Ni	mg kg ⁻¹	70	280	45	60	37	74	50	250	130	1500	100	400	45	150			
Pb	mg kg ⁻¹	70	350	40	200	100	200	100	500	120	1500	120	600	30	100			
Zn	mg kg ⁻¹	160	500	170	500	276	552	350	1750	700	10000	500	3000	375	1250			
total hydrocarbons	mg kg ⁻¹	14	36					300	1000									
Mineral oil	mg kg ⁻¹			50	1500													
Hexachlorobenzene	ug kg ⁻¹							2	6									
sum-DDT ²	µg kg ⁻¹			2.5	30													
DDT	µg kg ⁻¹							1	3									
DDE	µg kg ⁻¹							1	3									
DDD	µg kg ⁻¹							3	10									
sum 6 PAH ³	µg kg ⁻¹							1	3									
Naphthalene	µg kg ⁻¹	1.4-3.5	3.6-9	20	1000													
Phenanthrene	µg kg ⁻¹			50	1000													
Anthracene	µg kg ⁻¹			50	1000													
Fluoranthene	µg kg ⁻¹			20	1500													
Chrysene	µg kg ⁻¹			20	1000													
Benzo[a]anthracene	µg kg ⁻¹			20	1000													
Benzo[a]pyrene	µg kg ⁻¹			30	1000			0.05	0.5									
Benzo[k]fluoranthene	µg kg ⁻¹			30	1000													
Ideno[123cd]pyrene	µg kg ⁻¹			30	1000													
Benzo[ghi]perylene	µg kg ⁻¹			20	1000													
sum 7 PCBs	µg kg ⁻¹	2	2			500	1000	20	60	25	300	30	100					
PCB – 28	µg kg ⁻¹			1	30	25	50	2	6									
PCB – 52	µg kg ⁻¹			1	30	25	50	1	3									
PCB – 101	µg kg ⁻¹			4	30	50	100	2	6									
PCB – 118	µg kg ⁻¹			4	30	25	50	3	10									
PCB – 138	µg kg ⁻¹			4	30	50	100	4	12									
PCB – 153	µg kg ⁻¹			4	30	50	100	5	15									
PCB – 180	µg kg ⁻¹			4	30	25	50	2	6									
TBT	µg kg ⁻¹	3	7	(3) ⁴	(200) ⁴													
PCDD/F	WHO TEQ ng kg ⁻¹			20	500													

Notes to Table A6.15.

1) Data for Action Levels for England and Wales are currently being reviewed internally. They should be available shortly.

2) Sum DDT = DDT+DDD+DDE.

3) Sum 6 PAH = fluoranthene + benzo[b]fluoranthene + benzo[k]fluoranthene + benzo[a]pyrene + benzo[g,h,i]perylene + indeno[1,2,3-c,d]pyrene

4) In Finland, TBT values are provisional and based on organic tin

Table A6.16. Summary of preparation, digestion and extraction methods for assessment of dredged material (based on OSPAR SEABED 02/2/6 Rev.1-E(L)).

	Belgium	Canada	Denmark	England and Wales	France	Ireland	Netherlands	Norway	Northern Ireland	Portugal	Scotland Note 1	Spain	Sweden
Size fraction	< 63 µm		<2mm	< 2mm	< 2mm	< 2mm	< 2mm	< 2mm	<2mm	< 2mm	< 2mm	< 63 µm	
Metals	Total digestion		Total or partial Note 2	Partial HNO ₃	total digestion	Total (HF) Note 3	Partial (NVN 5770)	Total (HF) Note 3	Total (HF)	Total	Partial HNO ₃	Partial HNO ₃	
PAHs	ASE (high dw); soxhlet (low dw)			alkyl saponification	Hexane/CH ₂ Cl ₂		Acetone-SPE extraction	Soxhlet W/ dichloromethane	alkaline saponification	alkaline saponification	Sonication	Sonication cycle hexane/ dichloromethane	
PCBs				Solvent extraction		Soxhlet/ Solvent extraction		Acetone/hexane	hexane	Soxhlet/ Solvent extraction	Soxhlet	Sonication cycle hexane/ dichloromethane	
HCH				Solvent extraction		Soxhlet/ Solvent extraction		Acetone/hexane	hexane	Soxhlet/ Solvent extraction	Soxhlet		
DDTs				Solvent extraction		Soxhlet/ Solvent extraction		Acetone/hexane	hexane	Soxhlet/ Solvent extraction	Soxhlet		
Organotins	adding of acid, extraction with hexane/trop olone			Methanol hydroxide					iso-octane (EA)		Soxhlet	derivation Grignard	

Note 1 – Scotland - samples not sieved prior to determination of organics

Note 2 – Denmark – total or partial digestion of sediments determined at a local (county) level

Note 3 – Norway and Ireland - Hg determined after nitric acid digestion

Table A6.17. Dredged material classification criteria in Portugal. All concentrations in the <2mm size fraction.

<2mm fraction	Units	Class 1	Class 2	Class 3	Class 4	Class 5
		(clean)	(slightly contaminated)	(moderately contaminated)	(contaminated)	(very contaminated)
As	mg kg ⁻¹	<20	20-50	50-100	100-500	>500
Cd	mg kg ⁻¹	<1	1-3	3-5	5-10	>10
Cr	mg kg ⁻¹	<50	50-100	100-400	400-1000	>1000
Cu	mg kg ⁻¹	<35	35-150	150-300	300-500	>500
Hg	mg kg ⁻¹	<0.5	0.5-1.5	1.5-3.0	3.0-10	>10
Pb	mg kg ⁻¹	<50	50-150	150-500	500-1000	>1000
Ni	mg kg ⁻¹	<30	30-75	75-125	125-250	>250
Zn	mg kg ⁻¹	<100	100-600	600-1500	1500-5000	>5000
sum PCB	ug kg ⁻¹	<5	5 - 25	25-100	100-300	>300
sum PAH	ug kg ⁻¹	300	300-2000	2000-6000	6000-20000	>20000
HCB	ug kg ⁻¹	<0.5	0.5-2.5	2.5-10	10-50	>50

Table A6.18. Dredged material assessment criteria in The Netherlands. Concentrations in standard sediment consisting of 25 % clay (<2 um) and 10 % organic matter (1.7-2 × organic carbon).

	Parameter	Dredge material criteria CTT	Unit
Biological effects TEST	Crustacean (<i>C.volutator</i>)	35	Mortality % TU with grain size corrections TCDD TEQ pg/g dw
	Microtox SP (<i>V. fischeri</i>)	100	
	DR-CALUX	50	
Contaminants:	arsenic	29	mg/kg
	cadmium	4	mg/kg
	chromium	120	mg/kg
	copper	60	mg/kg
	mercury	1.2	mg/kg
	nickel	45	mg/kg
	lead	110	mg/kg
	zinc	365	mg/kg
	PAH total	8	mg/kg
	mineral oil	1250	mg/kg
	Sum 7 PCBs	100	µg/kg
	Sum DDT	20	µg/kg
	HCB	20	µg/kg

Table A6.19. Toxicity classes and sediment characterization for dredged material in Germany
(Ecotoxicological measurements are made in pore water and eluates).

Strongest dilution without effect	Dilution factor	PT value	Toxicity class	Characterization		Classification
			7-scale system	4-scale assessment	Description	
Original sample	2^0	0	0	0	unproblematic	category 1
1:2	2^{-1}	1	I	I		
1:4	2^{-2}	2	II	II		
1:8	2^{-3}	3	III	III	moderately critical	category 2
1:16	2^{-4}	4	IV	IV		
1:32	2^{-5}	5	V	V	highly critical	category 3
$\leq (1:64)$	$\leq 2^{-6}$	≥ 6	VI	VI		

ANNEX 7: INVENTORY OF NATIONAL SEDIMENT TREND MONITORING PROGRAMMES

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 by selecting/transferring 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.

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.

Questionnaire on sediment sampling

To help the OSPAR MON, a questionnaire was put forward to the participating countries. The objective of this was to supply MON/ICES with an overview of monitoring activities on sediment currently carried out or planned to be implemented in the different countries. For each of the above-mentioned sediment sampling strategies, the number of stations, cm of sediment material considered, year of programme start/next sampling round and whether data are reported to ICES are included, as well as fraction analysed. The results of the questionnaire are found as Table A7.1 in this report.

ANALYTICAL TECHNIQUES

For metal analysis, the detection by ICP-MS, ICP-OES or AAS techniques are of similar quality, apart from results close to the varying detection limits of the different techniques. It is therefore mainly of interest whether the digestion/fusion which brought the sediment to a fluid phase for introduction to the detector was total or partial.

For the organics, especially PAHs, the extraction technique can also be crucial for the extraction efficiency, and the use of high temperature systems/continuous extraction methods compared to room temperature shaking methods can yield incomplete extraction for the latter, with the largest difference for the more hydrophobic substances.

NORMALISATION

In order for the normalisation guidelines to be used in transportation bottom areas, it is necessary to measure Al, Li and TOC but also determine a pivotal point for each area, e.g., by analysing the sand grains after stripping of organic and clay particles. In sedimentation areas, the sediment usually can be regarded as “normalised” by nature, and a key normalisation parameter in this case is the dry matter content.

Questionnaire on analytical techniques

To help the OSPAR MON, a questionnaire was put forward to the participating countries. The objective of this was to supply MON/ICES with an overview of methods and parameters analysed within the monitoring programmes. The parameters and extraction techniques (as close as possible) are found in Table A7.2 of this report.

Overview of data currently held in the ICES database

This overview is based on a total search in the ICES database as of March 2003, extracting all data where more than one data set is available. It should be noted that all available data, without regarding QA status or release dates, have been used, so this is an upper estimate of available data.

Table A7.3 gives an overview of the time span for each parameter group, i.e., metals, PAH, PCB and others, and when last reporting of data to the data sets were done. Be aware that the time span is not an indication of the number of years for which samples have been analysed, as some samples are taken only every five years. Also, as the search was based on laboratories, some of the time spans can be longer if stations were transferred between laboratories.

Table A7.1. Inventory of methods for sediment monitoring - Questionnaire on sampling strategy.

Country	Core samples/ retrospective monitoring	Surficial sediments Stations	Surficial sediments regions	Suspended matter	Fraction used	others (specify)
Belgium	No	22 st.  10 cm, yearly 1991/2003	no	no	<63 µm (all) <2 mm (metals)	
Denmark	No	49 st.  2 cm, 5 year 2000/2003	no	no	<2 mm	no
France	8 st. ( 20–30 cm/1–3cm 10 yrs 1993/2003	Sediments move around	80–100 st. × 7 ( 1 cm, 10 years 1993–2003	no	<2 mm	one region sampled every year.
Finland	ca. 10 st ( 20 cm/1 cm 2003	No	no	only research	<2 mm	
Germany	not available at meeting	Not available at meeting	not available at meeting	not available at meeting	<20 µm (HM) (<63µm organic)	Many institutes, different methods
Iceland	Not at meetings	Not at meetings	Not at meetings	Not at meetings	Not at meetings	Not at meetings
Ireland	No	Under devel. ( Stations in regions to be repeated	5 regions (× 15st. each) ( 1 cm, 5 years 2001–2003	no	<2 mm (HM historical data) <63 µm (organics and HM)	One region sampled every year.

Under each heading no indicates not applicable, # stations,  if (to be) reported to ICES; for cores: target maximum depth and cm intervals for sampling; for surficial sediments: cm is centimetres of top layer sampled, and for both, years between sampling with first year/next year of sampling.

Table A7.1. Continued.

Country	Core samples/ retrospective monitoring	Surficial sediments Stations	Surficial sediments regions	Suspended matter	Fraction used	others (specify)
Norway	Cores taken for some stations	15–20 st.  1–2 cm, 5/10 year 1986–1997/2003	Early programme 1980	no	<2 mm	Number of stations depending on funding, sampling interval dependant on sedimentation rates at each station
Portugal	ca. 5 st 20–50 cm, 5 cm 1985/project based	C: 32 st. yearly E: 120 st. 4 year 5 cm, 1980/2003	no	no	<2 mm all < 63 µm (HM) < 20 µm (HM,2000)	also project based C: Coastline, E: Estuaries
Spain	No	60 st.  5 cm, yearly 1994/2003	no	no	<63 µm HM <2 mm organics	
The Netherlands	Project based 30–50 cm/1 cm 2001	ca. 60 st.  5 cm, 3 year 1990/2003	no	8 st.  SPM. 4 × year 1988	<63 µm	
United Kingdom	No	30-60 st.  1 cm, yearly 1999/	no	no	<63 µm all <2 mm if TT continues	Samples taken since 1994, but few analysed
Sweden	7 × 16 cores 80 cm/10 cm, 5 year 2003 upper 1 cm analysed or 5 upper laminae	16 stations.  1 cm, 5 year 1990/2003		one region, every 2 years 1989/2004	<2 mm	Also local coastal programmes. HELCOM-EGM programme. Cores stored for possible later analyses.

Under each heading no indicates not applicable, # stations,  if (to be) reported to ICES; for cores: target maximum depth and cm intervals for sampling; for surficial sediments: cm is centimetres of top layer sampled, and for both, years between sampling with first year/next year of sampling.

Table A7.1. Continued.

Country	Core samples/ retrospective monitoring	Surficial sediments Stations	Surficial sediments regions	Suspended matter	Fraction used	others (specify)
Poland		4 (7) stations  2003/2008			<2 mm	From HELCOM-EGM program
Latvia		3 stations  2003/2008			<2 mm	From HELCOM- EGM program

Under each heading no indicates not applicable, # stations,  if (to be) reported to ICES; for cores: target maximum depth and cm intervals for sampling; for surficial sediments: cm is centimetres of top layer sampled, and for both, years between sampling with first year/next year of sampling.

Table A7.2. Inventory of methods for national sediment monitoring - questionnaire on analytical strategy.

Country	Metals determined	Total/partial digestion	Organics determined	Extraction method	Normalisers and pivotal point (PP)
Belgium	Cd, Cu, Ni, Pb, Zn, Hg, As, Cr	Total (Partial Hg)	PAHs PCBs TBT (2003)	Soxhlet alk.soap.	Al, Li, TOC, <63 µm PP: metals (2 size fr.)
Denmark	Cd, Cu, Ni, Pb, Zn, Hg	Total (Partial Hg, Cd)	PAHs, Nonylphenol, DEHP PCBs, DDTs, HCHs, TBT	Soxhlet Soxhlet Soxhlet ethylation+cold extraction	Al, Li, LOI, TOC, <63 µm PP: no
France	Pb, Cd, Cu, Zn, Hg, Co, Ni, Cr, Ti, V		PAHs PCBs, DDTs, HCHs		Al, Li, LOI, TOC, CaCO ₃ , <63 µm
Finland	Zn, Pb, Cd, Cu, Zn, As, Hg, Cr, Ni (possibly ICP-MS)	Total (Partial Hg)	PAHs PCBs, DDTs		Al, Li, TOC, <63µm PP: no plans
Germany	Different labs	Different labs	Different labs	Different labs	Different labs
Iceland					
Ireland	Cd, Cu, Ni, Pb, Zn, Hg, Cr	Total (Partial Hg)	PCBs, DDTs, HCHs, OCPs (Toxaphenes) PAH, TBT, Brominated flame retardants.	Soxhlet/solvent extraction Ext. lab.	Al, Li, LOI, TOC, <63 µm; PP no
Norway	Zn, Pb, Cd, Cu, As, Hg, Cr, Ni	Total	PAHs PCBs, Possibly TBT	Soxhlet Soxhlet	Al, Li, TOC, <63 µm; PP: no
Portugal	Cd, Cu, Ni, Pb, Zn, Hg, Cr	Total (Partial Hg)	PAHs PCBs, THC	Soxhlet Soxhlet Direct extraction	Al, Li, Mn, Fe, TOC, LOI, <63 µm PP: metals (2 size fr.)
Spain	Cd, Cu, Ni, Pb, Zn, Hg	Partial (Aqua Regia)	PAHs PCBs, DDTs, HCHs HCB	Soxhlet	Fe, Mn, TOC, <63 µm PP: no

Table A7.2. Continued.

Country	Metals determined	Total/partial digestion	Organics determined	Extraction method	Normalisers and pivotal point (PP)
The Netherlands	Zn, Pb, Cd, Cu, Zn, As, Hg, Cr, Ni - now 70 elements	Partial	PAHs PCBs, TBT	Soxhlet (ASE) Soxhlet (ASE) ethylation+extraction	Al, Li, TOC, <63 and 2 µm PP: incl. uncertainty
United Kingdom	Zn, Pb, Cd, Cu, As, Hg, Cr, Ni	Total	PAHs PCBs		Al, Li, Fe, Mn, TOC, grain size PP: ??
Sweden	57 elements	total (partial Hg)	PAHs, PCBs, DDTs, HCHs, HCBs, chlordanes, TBT, Diphenylethers		Al, Li, TOC, grain size, CaCO ₃ PP:??

Under each heading: no if not applicable, for metals the individual metals (or no. if more than 10), for organics put each group of organics and extraction methods, for normalisation put each expected normaliser plus PP: status for pivotal points to be reported to ICES.

Table A7.3. Inventory of data held at ICES database.

Country	Years	Metals	PAH	PCB	Others
Belgium	max 10	13	2	18	14
2000	From 1–4 years	4	2	10	4
	From 5–6 years	1	0	5	2
	More than 6 years	8	0	5	8
Denmark	max 6	2	0	0	2
1991	From 1–4 years	1	0	0	1
	More than 6 years	1	0	0	1
Germany	max 16	77	10	22	79
2001	From 1–4 years	20	4	4	22
	From 5–6 years	11	6	9	11
	More than 6 years	46	0	9	46
Ireland	max 3	4	0	2	4
1995	From 1–4 years	4	0	2	4
Netherland	max 6	7	7	7	7
1990	From 1–4 years	1	1	1	1
	From 5–6 years	6	6	6	6
Norway	max 11	11	11	6	14
2000	From 1–4 years	1	4	1	4
	From 5–6 years	3	3	0	3
	More than 6 years	7	4	5	7
Poland	max 1	0	0	1	1
1990	From 1–4 years	0	0	1	1
Portugal	max 6	6	0	0	6
1990	From 5–6 years	6	0	0	6
United Kingdom	max 7	43	0	28	25
1999	From 1–4 years	23	0	11	25
	From 5–6 years	7	0	6	0
	More than 6 years	13	0	11	0

The first **(bold)** line indicates the maximum number of years and total number of samples for each country, with the last year of reporting indicated in the second line.

The next lines contain the number of stations with data for 1–4, 5–6 and 7 and more years. The years are defined as the span between first and last year sampled, e.g., 2 samplings with 5-year intervals will end up as 1 data set in the “From 5–6 years” row.

ANNEX 8: SEDIMENT DYNAMICS IN RELATION TO SEDIMENT TREND MONITORING

This working paper attempts to address the importance of sediment dynamics when interpreting temporal trend data on contaminants in sediments. In the paper several completely different areas are compared, the North Sea, the Baltic Sea. However, the present authors' knowledge is limited to these areas. Contributions on other areas, such as the St. Lawrence Gulf and Estuary and the Bay of Biscay are being drafted, and will be included at a later stage. Contributions from other areas will greatly improve the paper, and are invited.

For contributions or comments, please contact the authors, Hanneke Gieske (The North Sea) e-mail: j.gieske@nitg.tno.nl and Per Jonsson (The Baltic Sea) e-mail: per.jonsson@it.su.se

1 INTRODUCTION

Importance for interpretation of data

Time trends in contaminant, nutrient and carbon concentrations in sediments are usually inferred from sediment cores or from surface sediments taken at subsequent dates. Physical, chemical and biological processes can affect the concentration of contaminants, and should be taken into account when interpreting the data and preferably even in designing the monitoring schemes.

Physical processes include erosion, resuspension, transport and deposition. These processes are driven by different forces, such as isostatic movement, tidal and wind-driven currents, density currents, etc. For example, in the Baltic Sea increased eutrophication may lead to deep-water oxygen deficiency subsequently causing the creation of laminated sediments, and these apparently allow a strong down-core time control on contaminant input. However, these down-core trends may be distorted by several processes, including the increased input of clean sediment due to increased wind-driven erosion of glacial clays that are subject to isostatic uplift. In the North Sea the upper 10 cm in a sandy area may reflect contaminant input during the last months or even days, due to the constant reworking of the sediment, while in a muddy deposition area with a slow deposition rate the upper 10 cm of sediment may represent the situation of the last 25–50 years or more.

Chemical processes include early diagenetic processes, such as redox processes and authigenic formation of minerals. Inflow of oxic water to the Baltic Sea may cause changes from anoxic to oxic conditions, resulting in a release of easily mobilised metals, like Cd, to the water mass, possibly explaining the increased cadmium concentrations in biota at that time.

Biological processes include bioturbation, eutrophication and degradation of organic matter. Bioturbation in the muddy areas of the North Sea causes a strong mixing of the sediment, effectively obliterating down-core time trends. The oxic event described above in the Baltic Sea gave rise to benthic recolonization, causing bioturbation of the upper centimetres of the laminated sediments.

Below the processes and their effect on the sediment composition are elaborated for the North Sea and the Baltic Sea. These are subdivided into areas with different physical processes. There are several different systems to classify bottom types based on their physical and chemical properties. In this Annex, the following sediment classification system has been used according to (1):

- Accumulation areas are dominated by the continuous deposition of fine materials with grain sizes less than 0.006 mm.
- Transportation areas are characterised by a discontinuous deposition of fine particles/ aggregates, i.e., periods of accumulation are interrupted by periods of resuspension and transportation.
- In erosional areas erosion of sediment prevails.

Obviously any classification is a simplification of reality, and gradual changes between the three types may occur.

Description of the sediment dynamics and sedimentological characteristics

1. Accumulation areas

In the North Sea accumulation areas are small. The main depositional areas are the Oyster Grounds, the German Bight, the Outer Silver Pit, the Kattegat, the Norwegian Trench and Skagerrak. They are found in hydrodynamically quieter environments, below the fair weather wave base, where tidal currents are weak (e.g., near amphidromic points). Here muddy fine sands occur. Sedimentation rates are low, e.g., for the Oyster Grounds between 2 mm and 4 mm/yr.

2 “Transportational areas” (no net sedimentation or erosion)

In the **Dutch coastal zone** (down to 20 m water depth) waves and tides determine the hydrodynamic conditions. The sands are usually coarse with a mud content of maximum 1 to 2 %. At the upper shore face wave and storm action dominate. Near the shore a sand bar system occurs. When wave action is dominant the orbital water movement moves the sand grains to and fro, forming thin sediment laminae in the seabed. During storms waves stir up the sediment. After the storm the sand settles out, the coarse grains first, etc., resulting in a graded deposit, called storm deposit. At the deeper part of the foreshore, tidal currents move sand grains in the direction of the main axes of the tidal ellipse. The net residual current along a large part of the coast is directed towards the north (see Figure A8.1). Sand transport by tidal currents may result in thin, inclined (sometimes bi-directional) sediment layers. The interaction between waves, storms and tides results in complex sedimentological structures, and bioturbation often obliterates these completely.

In the **shallow shelf** (between 20 m and 30 m water depth) the hydrodynamic conditions are determined by tides and occasionally by storms. Here an extensive sand wave field occurs, with megaripples on one or both sides. These bed forms are formed by bed load transport of sand grains due to a uni-directional (residual) tidal current, whereby the sand grains are deposited at the lee side of the bed form. In some areas the sand waves migrate several metres per year in the direction of the net residual current (see Figure A8.1). In other areas, when ebb and flood current are of equal strength, the sand waves merely oscillate around the same position. The megaripples built up during summer on one or both sides of the sand waves, and are usually washed away during storms in the winter. The sand waves have typical lengths in the order of several hundreds metres to more than a km and heights of up to 8 m. The superimposed megaripples typically are several tenths of a metre long and several decimetres to 2 m high. In the seabed the formation of these bed forms results in thin inclined sediment layers, the so-called cross bedding. Occasionally storm waves may touch the seabed, and storm deposits may be formed. Sand banks occur too, but these do not seem to play a role in actual sediment transport.

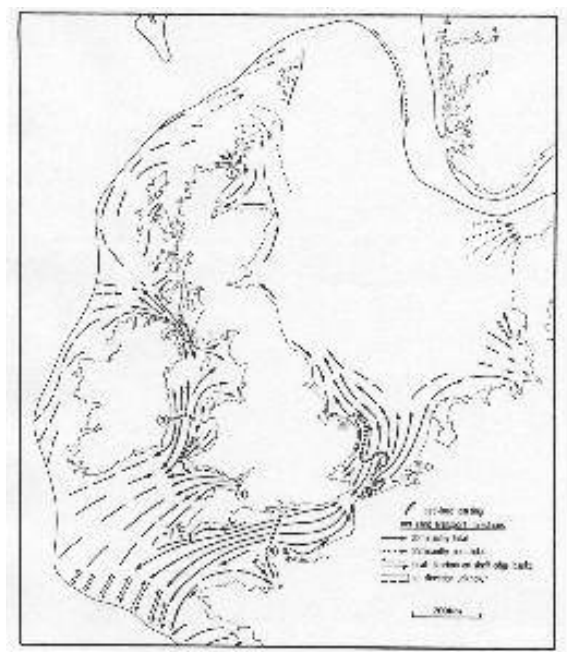


Figure A8.1. Net sand transport directions in the North Sea (Johnson *et al.*, 1982).



Figure A8.2. Circulation of water masses in the North Sea (OSPAR Quality Status Report, 2000). Locations of cores 98dw412, 417 and 421.

3 Erosional areas

Locally areas occur where net erosion takes place, exposing older, Pleistocene deposits at the sea floor. These erosional areas are found in the coastal zone as well as in the sand wave field.

Dynamic processes affecting the contaminant concentrations

- **Suspended matter transport**
Suspended matter is the main carrier of contaminants. Transport of suspended matter is closely related to the circulation of water masses in the North Sea due to residual tidal currents. See Figure A8.2. Sources of suspended matter include (estimates of different authors and QSR2000): Channel water (between 14 and 44 Mt/a), North Atlantic water (11–13 Mt/a), Baltic (0.5 Mt/a), erosion of English coast (Holderness: 1.4–2.6 Mt/a, Norfolk and Suffolk: 0.7–6.3 Mt/a), seafloor erosion (Flemish banks 1–2.4 Mt/a, all 9–13.5 Mt/a), input from rivers (4.8 Mt/a), primary production (1 Mt/a) and atmospheric deposition (1.6 Mt/a). In the more dynamic winter season concentrations of SPM are about twice those during the more quiet summer season.
- **Exchange of mud between the water column and the sediment in the transportational area**
The thickness of the “active layer”, i.e., the upper sediment layer that is reworked by wave and tide action, can be determined using its sedimentological and geochemical characteristics. The active layer usually shows a uniform concentration of Pb and Zn and Pb-isotopes ratio. The sediment layer below the active layer usually shows background concentrations for these components. In Figures A8.3a and A8.3b typical profiles for the sandy area are shown. It appeared that the active layer is usually between 15 cm and 40 cm in the “transportational area” (2). This suggests that the upper, most recently deposited sediment layer in the coastal area and sand wave field reflects the recent mud present in the water column. It is deposited in a faster time scale (days to months) than the time scale in which the contaminant load of the suspended mud changes.
- **Bioturbation in the depositional area**
Bioturbation occurs everywhere in the North Sea, but is especially important in muddy areas, such as the Oyster Grounds. In the muddy sediments of the Oyster Grounds a slow decrease to background concentrations at approximately 40 cm to 50 cm depth was found for Pb, Zn and the Pb-isotopes (2). This is attributed to bioturbation. In Figure A8.3c a typical profile for the depositional area is shown.
- **Redox status**
All sediments are oxic in the upper centimetres to occasionally 20 cm deep. Due to the low organic carbon content (in the sandy areas below 0.05 %, and in the depositional area below 1 %) the reduction capacity is relatively small, although remobilization of Fe and Mn at several cm depth occurs as well as formation of Fe and Mn-oxides at the sediment water interface (3). It is considered of minor influence on the concentrations of metals in the sediments.

Table A8.1. Characteristics of the North Sea sediments.

North Sea	Transportational area	Depositional area
Grain size	200–500 µm	100–150 µm
Mud content	0–2 %	10–50 %
C-org	0–0.05 %	0.1–1 %
Redox conditions	Upper cm to dm oxic	upper cm oxic
Dynamics	Upper 15–40 cm “mechanically” reworked	Sedimentation rate (Oyster Grounds 0.002 – 0.004 m/yr) Upper 40–50 cm bioturbated
Distribution of heavy metals	Homogeneous over active layer	Slow decline to background values

Implications for temporal trend monitoring

- **Transportational area.** Here the upper 15–40 cm reflects the latest quality status of the mud. Subsequent results can be used for time trend monitoring.

- Erosional areas. Results obviously should not be used in time trend monitoring of sediment quality, because time control of the results is very difficult, a.o., impeding a good correlation between input and sediment quality.
- Depositional areas. Here a very slow sedimentation and strong bioturbation hamper time trend monitoring. The sampling strategy must be adapted, e.g., sampling of upper few mm only.

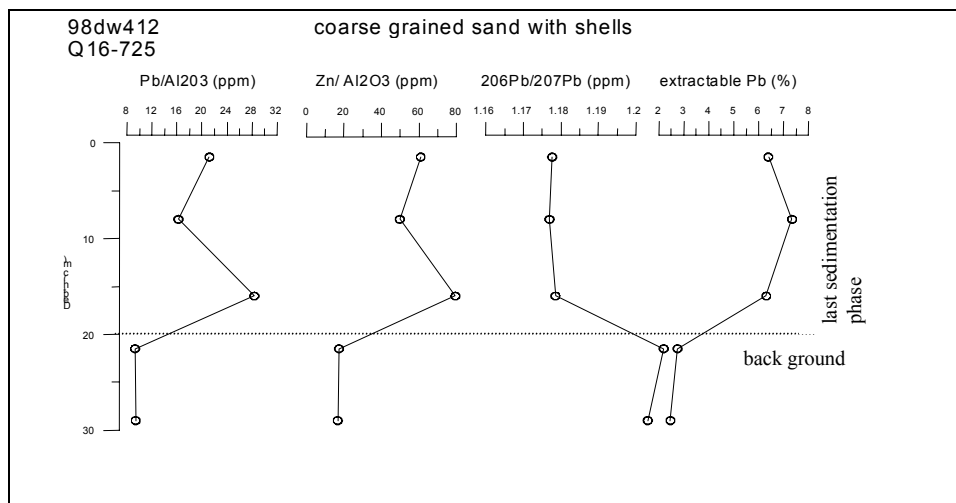


Figure A8.3a. Pb and Zn, normalised to Al₂O₃, and Pb-isotopic ratios in a core in the coastal area (transportational area).

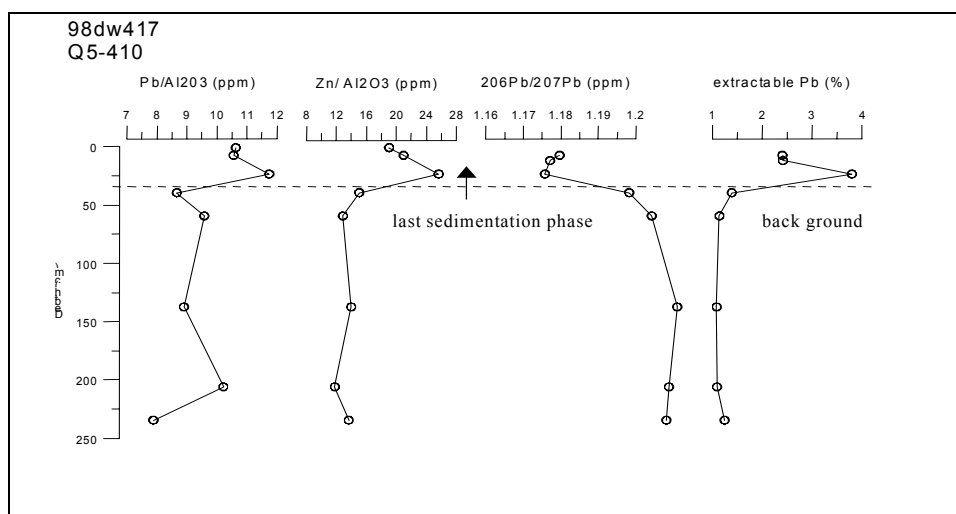


Figure A8.3b. Pb and Zn, normalised to Al₂O₃, and Pb-isotopic ratios in a core in the sand wave area (transportational area).

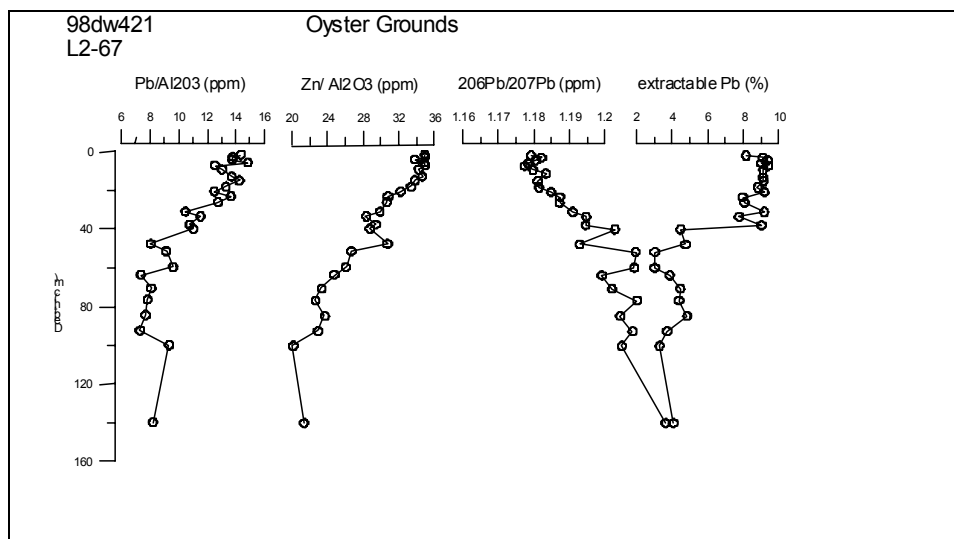


Figure A8.3c. Pb and Zn, normalised to Al₂O₃, and Pb-isotopic ratios in a depositional area (the Oyster Grounds).

4 THE BALTIC SEA

Erosion bottoms

In the Baltic Sea, erosion is a significant process not only in coastal areas but also in shallow offshore areas, in total estimated to constitute approximately 30 % of the bottom area. This percentage can vary within wide ranges in different parts of the Baltic Sea. In some areas in the southern Baltic erosion causes large damage to the shoreline in clayey/silty and sandy sediments.

In shallow waters near the coasts, (4) found that resuspension occurred during 15–35 % of the year, whereas in deeper areas, the bottoms were resuspended during less than 3 % of the year. (5) showed that resuspension in the Gulf of Bothnia decreased dramatically with increasing depth. Thus, bottom areas between 0–30 m had a mean annual resuspension frequency of >5 to 300 times per year. In deeper areas (>30–60 m) the bottoms as an average were resuspended 0 to 5 times per year.

Suspended matter derived from wave-induced resuspension has been shown to be of significant importance for the sedimentation process (e.g., 4–8). By using Al, Fe and Ti as markers to calculate the proportion of primary settling matter and resuspended sediment, (9) found that the resuspended portion commonly exceeded 50 % of the total sedimented matter in a coastal area of the Baltic Sea. (10) found on an average basis for the period of time 1969–1993 that erosion/resuspension accounts for 70 % of the deposited matter in the open NW Baltic Proper approximately 50 km south of the area investigated by (9). During individual windy years, the eroded/resuspended portion may increase to 85 %.

* Eroded matter constitutes a major part of what finally is sedimenting in the deep depositional areas

Transportation bottoms

Approximately 40 % of the bottom area of the Baltic Sea is classified as transportation bottoms. The transportation bottoms may be characterised as the transition zone in which eroded/resuspended sediments are transported to the final accumulation areas in the deep offshore bottoms of the Baltic. Due to the large share of erosion and transportation bottoms (2/3 in the Baltic Proper), one has to keep in mind that the delay time for contaminant changes to be manifested in the deep accumulation areas may be substantial (11). A contaminant-carrying particle, finally buried in the offshore depositional areas, may have passed a number of resuspension events before being trapped in the anoxic sediments years to decades after dispersion into the sea. Particle-associated contaminants may be retained in long-term transportation bottoms until strong energy input from waves, currents or sub-marine slides resuspend the sediments years to decades after the first deposition.

* Temporary accumulation in transportation bottoms may delay contaminant changes in the deep depositional areas

Areas of accumulation

Compared to the North Sea, large areas of the Baltic Sea are classified as accumulation areas for fine material. Although it may vary in different parts of the Baltic Sea, in offshore areas as an average 30 % of the bottom area is considered to

constitute this type of bottom. In general, accumulation bottoms are found at greater depths than 75–80 m, although in more shallow areas accumulation can occur in topographic depressions also up to 50 m in wind-exposed areas. The accumulation rate in the surficial sediment is generally between 1 mm and 4 mm.

The accumulation areas may then be divided into: 1) bioturbated sediments, and 2) azoic laminated sediments. In the bioturbated sediments animals are causing a more or less effective mixing of the upper sediment column ranging from in the order of millimetres to several decimetres. Concentration profiles in the sedimenting matter may subsequently become more or less obscured due to the abundance and bioturbating efficiency of the benthic fauna.

Table A8.2. Brief characteristics of the Baltic Sea accumulation sediments.

The Baltic Sea	Depositional areas
Grain size	Mainly < 60 µm
Mud content	>90 %
TOC content	2–10 %
Redox conditions	Upper cm temporarily oxic, temporarily anoxic
Dynamics	Sedimentation rate offshore: mean 1-3 (range 0.5–20) mm/yr Sedimentation rate archipelago: mean 17 (range 1–70) mm/yr

Lack of bioturbation causes laminated sediments

In sediments with normal oxygen conditions the benthic fauna bioturbates the sediment resulting in a more or less homogeneous sediment without any clear structures. In areas with poor oxygen conditions (< 2 mg O₂/l) causing elimination of the benthic fauna, often laminated sediments are created. Without the bioturbating macrobenthic fauna, the normally occurring seasonal changes in the composition of sedimenting matter are preserved in the sediments as more or less distinct annual varves or lamina. In the Baltic, the high resuspension of minerogenic particles deriving from glacial and post-glacial clays during the winter period normally is manifested by a light layer followed by a darker (often black) layer with a higher organic content, representing the spring and summer season.

The extinction of the benthic fauna is normally a more or less gradual process. In the sediments this often can be seen as a few, more or less diffuse, lamina overlaying a homogeneous bioturbated sediment (Figure A8.4). Often this is followed by a bioturbated layer, indicating a shorter or longer period of suitable conditions for the benthic fauna. Finally this development is characterised by distinct lamination often to the top of the sediment column.

In the Baltic Sea several studies have demonstrated highly variable average sediment accumulation rates in deep areas (Table 2; 9, 12–14). Although these investigations showed that sediment accumulation rates vary over time and among areas, most estimates are given as averages over a period of time ranging from decades to thousands of years.

In the deepest parts of the major basins of the open Baltic Proper, laminated sediments have been deposited at anoxic bottoms for more than a hundred years, indicating natural oxygen deficiency in these areas (8). During recent decades, the prerequisites for detection of inter-annual changes of contaminant burial have been substantially improved over large areas in the Baltic Proper due to a large-scale expansion of anoxic/hypoxic laminated sediments (8). The area of laminated sediments has expanded since the 1940s, and in the late 1980s approximately one third of the Baltic Proper at depths exceeding 75–80 m had surficial laminated sediments. During the 1960s and early 1970s, as an average, a bottom area of approximately 3,000 km² was wiped out from macrobenthic fauna annually. This has been attributed to a substantial increase in sedimentation of autochthonous organic matter due to increased eutrophication of the Baltic Sea (15).

Due to a significantly better time resolution laminated sediments may be considered much more sensitive to pollution load changes than bioturbated sediments. In areas where both types occur, it is suggested that the laminated sediments are best suited for temporal trend monitoring.



Figure A8.4. A typical laminated sediment from the open Northern Baltic Proper. *In situ* image taken with a sediment profile imaging camera from 125 m depth. The total length of the image is approximately 10 cm.

However, also when using laminated sediments for monitoring, it is important to bear in mind that the lamination is not a static phenomenon. In 1993, a major inflow of saline water occurred through the Danish Sounds into the Baltic Sea, which deepened the halocline in the northern Baltic Proper to the extreme depth of 110–120 m, and improved the near-bottom oxygen concentrations (16) over large areas above this depth level. The oxygenation of the sea floor allowed benthic fauna to recolonize, causing bioturbation down to a couple of centimetres below the sediment surface. During the rest of the 1990s up to present (2002), anoxic/hypoxic conditions in the deep water have caused mass mortality of benthic fauna in the recently colonised areas again leading to an expansion of the laminated area. The oxic episode after 1993 may be seen in the sediment column as a 1–2 cm thick bioturbated layer, over-layered by laminated sediments.

* Due to the lack of macrobenthic fauna and subsequently low bioturbation in the laminated sediments, the time resolution for contaminant changes is high in this type of sediment.

* Also laminated sediments are subject to delay of contaminants in the transportation zone

Isostatic processes cause resuspension of large amounts of clean masses

It has been shown that the isostatic land up-lift after the latest glaciation of Scandinavia is causing large relocation of material (6, 8). By this land up-lift, bottom areas formerly below the wave-base are gradually exposed to wave action and large quantities of glacial and post-glacial clays are eroded. Estimations yield that 50–80 % of what is finally settling out in the deep areas of the Baltic derives from this process (8–10, 17) and the inter-annual changes are significant.

* Anthropogenic input of nutrients and contaminants is diluted by a large input of uncontaminated eroded old clays.

Storm-induced erosion causes changed sediment accumulation rates

From long-term registration of waves along the German Baltic coast it has been shown that the annual frequency of storm waves increased from 1831 to 1990, with substantial differences between years and decades (18). Based on detailed studies of laminated sediment cores from the NW Baltic Proper, (10) found that the sediment accumulation rate varied substantially between years/decades (Figure A8.5). By comparing the variation in sediment accumulation rate with wind speed measurements obtained from a nearby weather station they demonstrated a high relationship between dry matter deposition and a wind speed frequency of $\geq 14 \text{ m s}^{-1}$ expressed as annual means.

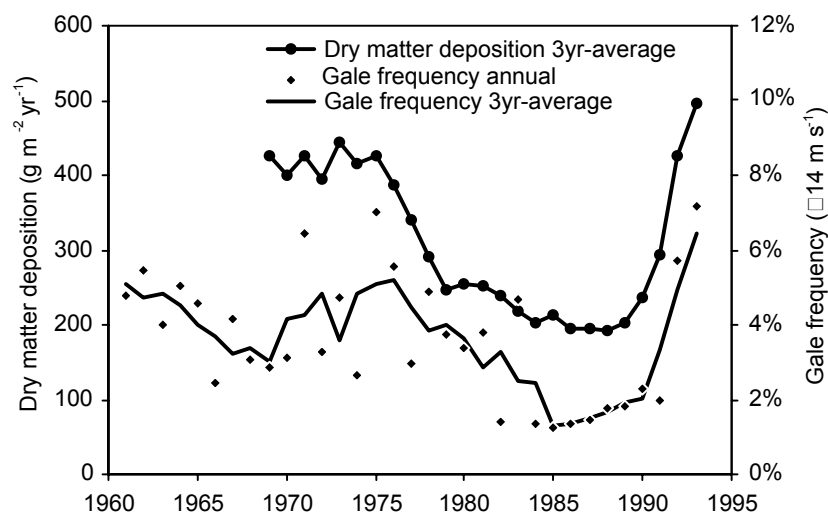


Figure A8.5. Dry matter deposition (3-year running mean) in a core mean ($n=3$) and the frequency of wind velocities ≥ 14 m/s (gale force; individual years and 3-year running mean) for the period 1969–1993. (From 10).

In the Baltic proper, the 1950–1970s was characterized by higher frequency of gale forces than in the 1980s. In the early 1990s the gale frequency increased dramatically reaching a maximum in 1993 when a large salt-water intrusion occurred from the Kattegat into the Baltic. Also the dry matter deposition rates were significantly higher in the 1970s and in the early 1990s than in the 1980s, which may be considered as a calm decade in this area. The authors suggested that sediment accumulation rates can be predicted in offshore areas of NW Baltic Proper from the obtained relationship.

In a recent study in the Swedish St. Anna archipelago (19) found a high correlation between dry matter deposition and gale frequency. Also recent studies in Stockholm archipelago, Sweden, indicate close links between high wind velocities and high sediment accumulation rates. However, concerning other areas than the N Baltic Proper, different time trends certainly exist. Although inter-annual changes in sediment accumulation rate are difficult to detect in sea areas where bioturbated sediments prevail, it is likely that similar variations occur in these areas. The bioturbation is likely to obscure these variations.

* Sediment accumulation rate is substantially increased during stormy years

* Changes in storm frequency may be used to indicate whether extra care should be taken when interpreting temporal trend monitoring

* Only if the frequency of storms is constant throughout the monitoring period may conclusions be drawn.

Resuspension of old clays affect sediment carbon content

In numerous investigations it has been shown that the sediment carbon content is of great importance for the sediment burial of especially hydrophobic organic contaminants. Therefore processes/mechanisms that may alter the organic carbon content have to be taken into consideration in trend monitoring.

On the same cores as referred to in (10), also TOC was analysed. In Figure A8.6 it is demonstrated that the dry matter accumulation rate decreased by approximately 50 % in the 1980s, which corresponded to a TOC content increase from 3–4 % to 7–8 % during the same period of time. When the dry matter deposition rate increased in the early 1990s the carbon content decreased. The interpretation of this is that the erosion/resuspension of mainly minerogenic matter from glacial and postglacial clays increases during windy years, whereas the carbon input from primary production becomes more dominant during calm years with low dry matter sedimentation rates.

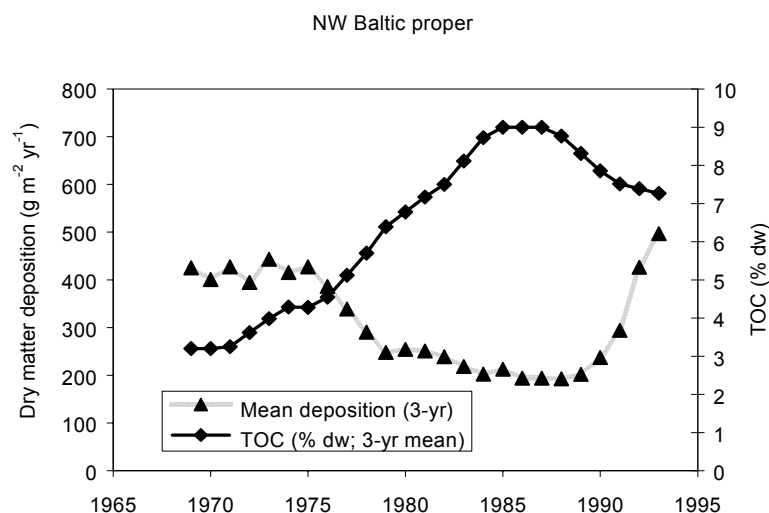


Figure A8.6. Dry matter deposition and TOC content versus time. 3-year running average of the core means. (From 10 and 20).

* Wind-induced changes in sediment accumulation rates may substantially change the organic content of the sediment

Chemical redox processes

Metals

(17) suggested that the occurrence of laminated sediments in the offshore Baltic Proper caused increased trapping of contaminants (metals and organic pollutants) in the sediments. Although these mechanisms are not fully understood, changes in burial efficiency need to be taken into account when interpreting time trends in laminated sediments.

Remobilization processes within the sediment may cause interpretation problems. On the basis of renewed sampling of two sampling sites in the Baltic Proper with an interval of 12 years, (21) found differences in vertical distribution for especially zinc, indicating mobilization processes within the sediment. Therefore, detailed interpretation of retrospective trace element studies of Baltic sediments should be considered with due reservation.

Redox changes may cause differences in trapping efficiency of metals. This is a well-known phenomenon for a number of elements, e.g., iron and manganese. Also trace metals like Cd, Pb, Zn, Hg and Cu have shown to be more effectively sequestered in anoxic Baltic sediments. (22) found high correlations between all these metals and the degree of anoxia described as area of laminated sediments, which indicates increased redox-induced trapping for these sulphide-binding metals in the laminated sediments. At sites where continuous lamination has occurred for hundreds of years, the metal concentrations have gradually increased without any steep increases during recent decades. As no dramatic redox changes seem to have occurred in the naturally laminated bottoms, sediment cores from this type of bottom probably contain the best retrospective information about the pollution history of metals in the Baltic Proper.

During the ICES/HELCOM sediment baseline study substantially lower concentrations of these metals, especially Cd, were detected in surficial sediments in the Northern Baltic Proper in June 1993 (23). In the early 1990s gradually larger salt-water inflows from the Kattegat were registered reaching a maximum in January 1993, leading to substantially improved oxygen conditions in the deep water down to 115–120 m (16). The change from anoxic to oxic conditions with a subsequent recolonisation of benthic fauna obviously caused release of the easily mobilised metals, e.g., Cd, to the water mass. In the 1990s increased cadmium concentrations have been detected in biota along the Swedish coast of the Baltic Proper (24). This increase may to a certain extent have been caused by mobilisation of cadmium from the sediments.

- * Continuously laminated sediments constitute the best historical archives;
- * Substantial changes of metal concentrations occur as a result of changing redox conditions;
- * Mobilisation of metals may cause substantial concentration changes in biota.

Organic compounds

Sediment profiles of chlorinated compounds (e.g., EOCs, PCBs, DDTs, PCDD/Fs) indicate substantially increased sequestering in the Baltic Proper sediments from the 1950s and onwards, coinciding in time with the expansion of laminated sediments and clearly increasing organic content in the sediments (17, 25-26). From these studies it is indicated that the sequestering efficiency, due to the turnover from oxic conditions to hypoxia/anoxia close to the sediment/water interface, has increased in the sediments. A pilot study aiming at comparing the burial efficiency of PCBs in laminated sediments with bioturbated sediments from the Stockholm archipelago (20) showed as an average 40 % increase in concentrations when the sediment turned from bioturbated to laminated conditions. This may be attributed to increased eutrophication causing stagnant conditions in the near-bottom water.

* Organic compounds are more effectively trapped in anoxic azoic sediment

References

1. Håkanson, L. and Jansson, M. 1983. *Principles of lake sedimentology*. Springer-Verlag, Berlin, 316 pp.
2. Gieske, J.M.J., Van Os, B.J.H. and van der Spek, A.J.F., 1999. Determination of mixing depth of North Sea sediments by means of geochemical and sedimentological analyses. Report nr. NITG 99-196B, Netherlands Institute of Applied Geoscience TNO
3. Slomp C.P., 1997. Early diagenesis of phosphorus in continental margin sediments. Thesis Wageningen University.
4. Christiansen, C., Gertz, F., Laima, M.J.C., Lund-Hansen, L.C., Vang, T. and Jørgensen, C. 1997. Nutrient (P,N) dynamics in the southwestern Kattegat, Scandinavia: sedimentation and resuspension effects. *Environmental Geology* 29, 66-77.
5. Brydsten, L. 1993. Characterization of transport bottoms in the Gulf of Bothnia – A model approach. *Aqua Fennica* 23, 153-164.
6. Axelsson, V. and Norrman, J.O. 1977. Tillförsel, omlagring och deposition av sediment vid Sveriges kuster och i omgivande hav. In: *Havet naturförhållanden och utnyttjande, Fysisk Riksplanering (FRP)*, Bostadsdepartementet, 7(5). (In Swedish).
7. Brydsten, L. 1990. Distribution of organochlorine compounds bound to sediments in the Baltic Sea. In: *Commission of the pollution research reports, Transport of organic micropollutants in estuarine, marine and brackish waters*. Wahlberg, C., Minderhound, A. and Angeletti, G. (eds). pp. 33-44.
8. Jonsson, P., Carman, R. and Wulff, F. 1990. Laminated sediments in the Baltic - A tool for evaluating nutrient mass balances. *Ambio* 19, 152-158.
9. Blomqvist, S. and Larsson, U. 1994. Detrital bedrock elements as tracers of settling resuspended particulate matter in a coastal area of the Baltic Sea. *Limnology and Oceanography* 39, 880-896.
10. Eckhéll, J., Jonsson, P., Meili, M. and Carman, R., 2000. Storm influence on the accumulation and lamination of sediments in deep areas of the northwestern Baltic Proper. *Ambio* 29, 238-245.
11. Jonsson, P., 2000. Sediment burial of PCBs in the offshore Baltic Proper. *Ambio* 29, 260-267.
12. Östlund, P. and Hallberg, R.O. 1991. Plutonium in sediments - Apparent half-lives. *Environmental Geology and Water Science* 17, 195-200.
13. Kunzendorf, H. and Christiansen, C. 1997. Estimation of recent sedimentation histories in the Gotland basin using cores from the GOBEX study. In: *Proceedings of the Fourth Marine Geological Conference – the Baltic*. Cato, I. and Klingberg, F. (eds). Sveriges Geologiska Undersökning, Uppsala, 1995, pp. 111-116.
14. Neumann, T., Christiansen, C., Clasen, S., Emeis, K.-C. and Kunzendorf, H. 1997. Geochemical records of salt-water inflows into the deep basins of the Baltic Sea. *Continental Shelf Research* 17, 95-115.
15. Jonsson, P. and Carman, R. 1994. Changes in sediment deposition of organic matter and nutrients in the Baltic Sea during the twentieth century. *Marine Pollution Bulletin* 28, 417-426.
16. Baltic Marine Environment Protection Commission - Helsinki Commission - 1996. *Third Periodic Assessment of the State of the Marine Environment of the Baltic Sea, 1989-1993*; Background Document. Baltic Sea Environment Proceedings No. 64B
17. Jonsson, P. 1992. Large-scale Changes of Contaminants in Baltic Sea Sediments during the Twentieth Century. *Acta Universitatis Upsaliensis. Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science*, 407. Uppsala, Sweden. ISSN 0282-7468, ISBN 91-554-2997-1, 52 p.
18. Baerens, C. and Hupfer, P. 1994. On the frequency of storm surges at the German Baltic coast. In: *Proceedings, of 19. Conference of Baltic Oceanographers*. Gdansk, Poland, pp. 311-317.
19. Persson, J. and Jonsson, P. 2000. Historical development of laminated sediments – An approach to detect soft sediment ecosystem changes in the Baltic Sea. *Marine Pollution Bulletin* 40, 122-134.

20. Jonsson, Per, Stockholm University, ITM, Stockholm, Sweden, unpubl. data.
21. Tervo, V. and Niemistö, L., 1989. Concentrations of trace metals, carbon, nitrogen and phosphorus in sediments from the northern parts of the Baltic Sea. International Council for the Exploration of the Sea. C.M. 1989/E:7, Marine Environment Quality Committee. 14 pp.
22. Borg, H. and Jonsson, P., 1996. Large-scale Metal Distribution in Baltic Sea Sediments. *Mar. Pollut. Bull.* 32, 8-21.
23. Perttilä, Matti, Finnish Institute of Marine Research, Helsinki, Finland, pers.comm.
24. Bignert, A., 2001. Comments concerning the National Swedish Contaminant Monitoring Programme in marine biota. Contaminant research group at the Swedish Museum of Natural History, Annual status report to the Swedish Environmental Protection Agency, 2001. 122 p (mimeo).
25. Niemistö, L. and Voipio, A., 1981. Notes on the sediment studies in the Finnish pollution research in the Baltic Sea. Rapp. P.-v. Réun. Cons. int. Explor. Mer, 181:87-92. 1981.
26. Perttilä, M. and Haahti, H., 1986. Chlorinated hydrocarbons in the water and sediments of the seas around Finland. Publications of the Water Research Institute, National Board of Waters, Finland, No. 68:197-200.

ANNEX 9: MEASUREMENTS IN RELATION TO (BIO-)AVAILABLE CONCENTRATIONS OF CONTAMINANTS IN SEDIMENTS

In this document only the bioavailability of hydrophobic contaminants is discussed. To characterize the bioavailability of contaminants in sediment it is important to agree from the onset on the exact meaning of bioavailability. For a biologist bioavailability is the amount of contaminant that can be taken up by an organism through exposure to contaminated sediment. The sediment chemist is looking at bioavailability from the viewpoint of binding properties of the contaminants in sediment i.e., what is or can be released from the sediment. From that chemical perspective, two parameters, being the “**free dissolved**” and “**water-extractable**” concentration, can describe the availability of contaminants in sediment for transfer to another phase. To avoid confusion with biologists about terminology, it is perhaps better to leave out “bio” and speak about “**availability**”. It is also a better approximation to reality as the parameters above are not only relevant for uptake by biota, but also the driving forces for diffusive transport, release from and uptake by the sediment. Both parameters and their meaning are described in more detail in what follows.

Freely dissolved concentrations

Freely dissolved concentrations refer to the concentration of molecules that are not bound to colloids, sediment particles nor to other sediment constituents. Such freely dissolved molecules are often considered to be the “effective concentration” for toxicity, bioconcentration and diffusive transfer into other media. The free-dissolved concentration does not necessarily relate to the concentration in the sediment. A low free-dissolved concentration can be the result of low concentrations in the sediment but also of a very strong binding of the contaminants to the sediment.

Freely dissolved concentrations are directly proportional to the contaminant **fugacity** in the sediment. Fugacity is the tendency of a substance to escape from a medium into other media and it is equivalent to the **chemical potential**. The term fugacity was introduced by Lewis¹ in 1901, and Don Mackay has later on introduced it to the environmental field². Fugacity is expressed in Pascal and its reference medium is the gaseous phase. Fugacity is an important measure of availability, because it drives the diffusion from one medium into other environmental media³ and, by definition, from high to low fugacity. Therefore, fugacity also drives the diffusion into organisms thereby determining the equilibrium concentration in biota⁴. Thus, fugacity and, as a result, freely dissolved concentrations are important measures of (bio)availability³.

Also, sediment quality criteria are often derived from aquatic toxicity data that were recalculated to sediment concentrations using partition coefficients. For the sake of risk assessment it seems therefore logical to measure the freely dissolved concentration in interstitial water and compare that result directly with the waterborne quality standard. Furthermore, the freely dissolved concentration (and fugacity) is an indicator for the diffusive pressure of contaminants into the immediate aqueous environment.

The estimation of fugacities and dissolved pore water concentrations is often based on the partition coefficient and (total) contaminant concentrations in the sediment expressed on organic carbon⁵. This can lead to substantial uncertainties⁶ and they should therefore preferably be measured instead of estimated.

Water extractable sediment concentration

The “water extractable concentration in the sediment” is a term that describes the quantity of a pollutant that in time can become available in its dissolved form. It represents therefore the amount that can be released by depletive processes, resulting in zero or minimal water concentrations. In the environment such processes occur by various deposit-feeding invertebrates that feed on sediment particles, and are releasing a large part of the particle-bound contaminants from the sediment that can then be taken up through the gut of the animals^{7,8}. Also, bacterial communities can deplete the dissolved pore water fraction, which then leads to a release from the sorbed fraction. Digestive processes within deposit feeders are rather complicated, and the same holds for biodegradation by bacterial communities. Nevertheless, the overall process is the same, a depletion of the available forms and the subsequent release from bound forms.

This depletion of available forms from the sediment can also be the result of abiotic processes such as washing out or uptake by sorption material. The endpoint is particularly suited to indicate the concentrations that are available for transfer to other phases. If “total” concentrations obtained by ASE or soxhlet are significantly higher than “available” ones, this will indicate that the remaining amount of contaminants is irreversibly bound to the sediment.

Measurement approaches

Partitioning into polymers can be used to measure the parameters described above. In 1996, polymer-coated glass fibres were already applied to determine “freely dissolved concentrations” of phenols in aqueous samples⁹. This method was specifically designed to ensure “negligible depletion” of the freely dissolved concentration, and such extraction techniques are thus referred to as negligible depletion solid phase micro-extraction (nd-SPME). Recently, SPME has been extended to the measurement of freely dissolved concentrations in dense environmental matrices such as

sediment^{10,11}, and it is then referred to as matrix-SPME. The basic principle of such methods is very similar to the proper usage of a **thermometer**¹². You stick the thermometer in the medium, wait until the temperature is equal to that of the medium (in equilibrium) and you read the temperature. Likewise a reference device is brought in equilibrium with the medium of which you want to know the pollution level and you read the pollution level from the device. Questions such as “what unit, how to compare readings?” are actually just a matter of convention equal to reading the temperature from a thermometer. A similar approach can be used to measure the freely dissolved concentration by using “equilibrium sampling devices” or ESDs¹².

1. The ESD is placed in the sample until thermodynamic equilibrium is attained.
2. The amount of contaminant extracted by the ESD is determined (e.g., by GC or HPLC)
3. The freely dissolved concentration can then be calculated according to: $C_{\text{water}} = C_{\text{ESD}} / K_{\text{ESD,water}}$ (Formula 1).

Several ESDs are presently available. ESDs based on SPME use a piece of polymer-coated optical fibre, which is brought directly into a sediment sample for an equilibrium enrichment of contaminants into the polymer coating. The fibre is subsequently inserted into the injector of a gas chromatograph, where the pollutants are thermally desorbed and the concentration in the polymer directly measured. Silicone rubber films (SRF) are another promising ESD. They represent a larger sampling phase, and are very suitable for extraction with various solvents. The SRF approach requires only the standard laboratory equipment normally used for sediment analysis and can be combined with traditional clean-up procedures (e.g., removal of sulphur). It applies therefore to virtually all hydrophobic contaminants ($\text{Log } K_{\text{OW}} > 3$). The present methods are limited to $\text{Log } K_{\text{OW}}$ of about 7 as equilibrium times become too long for higher values.

Also, “water extractable sediment concentrations” are measurable by diffusive sampling¹³, when using a sampling phase with a large sorption capacity that continuously traps all dissolved molecules. Just as dry weight of sediment is generally determined by drying a sediment sample until constant weight, i.e., until no more water escapes the sample, the ESD will extract the contaminants out of the sediment through the water phase until depletion. The first methods were based on the mixing of sediment with small sorbent particles (Tenax), which in turn requires the separation of sorbent particles from the sediment prior to extraction and measurement. Silicone rubbers can also be applied for this approach, which simplifies the separation of sediment and sampler.

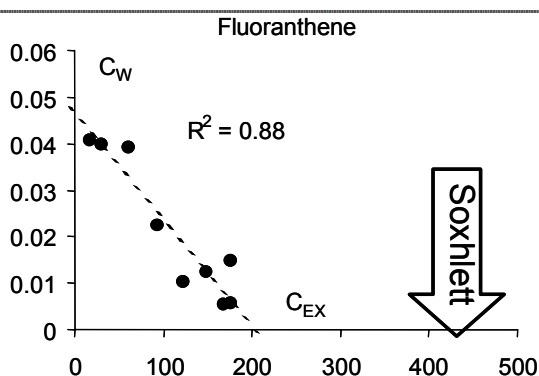


Figure A9.1. Plot of C_w ($\mu\text{g/L}$) versus extracted content, C_{EX} ($\mu\text{g/kg}$). The arrow indicates the content measured by Soxhlet extraction of the sediment

Procedure

Solid Phase samplers (SPS) of silicon rubber (typically 100 cm^2 and 0.05 cm thick) are pre-extracted with ethyl acetate in a soxhlet. Cleaned SPS are exposed to sediment in glass bottles at varying weight ratios of 0.01 to $1 \text{ g SPS/g sediment}$. Minimum sediment content in suspension was 0.10 g/ml . After 23 days incubation at an orbital shaker (150 rpm , 3 cm amplitude) SPSs are washed with water and extracted using soxhlet. After cleanup the extract is analysed by HPLC. The freely dissolved concentration (C_w) is estimated with the pre-determined SPS-water partition coefficient ($K_{\text{SR,W}}$). The extracted fraction (C_{EX}) is calculated from the amount extracted by the SPS divided by the amount of sediment present. A plot of the extracted concentration (C_{EX}) versus the corresponding C_w , allows extrapolation to $C_{\text{EX}}=0$ which gives original C_w . Likewise extrapolation to $C_w=0$ will give a value for the maximal extractable content ($C_{\text{EX,MAX}}$).

At the working group meeting, a method was presented where the two methods of sampling (equilibrium and depletive) were integrated into one approach. The phase ratio between the mass of sampling phase and mass of sediment is varied, going from “negligible depletion” to “full depletion”. The results from such an approach are shown in Figure A9.1.

As above, the concentration in the water phase is calculated according to formula 1. The $K_{\text{ESD,water}}$ can separately be determined for any applied reference phase. By relating the concentration extracted from the sediment to the determined concentration in the water phase, a value for maximum depletion can be obtained by extrapolation to zero concentration in the water phase. Extrapolation to zero sediment extraction results in the freely dissolved concentration in the water phase for a non-depletive situation. The methodology allows the determination of both parameters, “**free dissolved**” and the “**water extractable**” concentration each being highly relevant for comparative risk assessments.

Implications within a monitoring context

The ultimate goal is to introduce both measurements in routine monitoring programmes as a tool to assess the availability of hydrophobic organics in the environmental matrices. The described methods are widely applicable to sediments and the results do not require normalisation for differences in sediment composition. In fact these methods can be seen as analytical normalisation procedures that apply silicone rubber as an analytical reference material. This analytical normalisation procedure allows the direct comparison of sediments of different composition. These methods will thus facilitate comparisons of contamination levels within and between geographical areas.

Finally, it should be noted that these methods are not intended to replace total concentration measurements. They are rather thought to provide complementary and very useful information.

References

1. Lewis, G. *Am Acad* 1901, 37, 49-69.
2. Mackay, D. *Environmental Science and Technology* 1979, 13, 1218–1223.
3. Mayer, P. 2000. Partitioning based approaches to study exposure and effects of hydrophobic organic substances. Ph.D. thesis. Utrecht University Utrecht. 120.
4. Wilcockson, J. B.; Gobas, F. A. P. *Environmental Science & Technology* 2001, 35, 1425–1431.
5. Ditoro, D. M.; Zarba, C. S.; Hansen, D. J.; Berry, W. J.; Swartz, R. C.; Cowan, C. E.; Pavlou, S. P.; Allen, H. E.; Thomas, N. A.; Paquin, P. R. *Environmental Toxicology and Chemistry* 1991, 10, 1541–1583.
6. tenHulscher, T. E. M.; vanNoort, P. C. M.; vanderVelde, L. E. *Chemosphere* 1997, 35, 2331-2344.
7. Forbes, V. E.; Forbes, T. L. *Environmental Toxicology and Chemistry* 1997, 16, 1002–1009.
8. Forbes, V. E.; Andreassen, M. S. H.; Christensen, L. *Environmental Toxicology and Chemistry* 2001, 20, 1012–1021.
9. Vaes, W. H. J.; Urrestarazu Ramos, E.; Verhaar, H. J. M.; Seinen, W.; Hermens, J. L. M. *Analytical Chemistry* 1996, 68, 4463–4467.
10. Mayer, P.; Vaes, W. H. J.; Hermens, J. L. M. *Analytical Chemistry* 2000, 72, 459–464.
11. Mayer, P.; Vaes, W. H. J.; Wijnker, F.; Legierse, K. C. H. M.; Kraaij, R. H.; Tolls, J.; Hermens, J. L. M. *Environmental Science & Technology* 2000, 34, 5177–5183.
12. Mayer, P.; Tolls, J.; Hermens, J.; Mackay, D. *Environmental Science and Technology*. Feature section. 2003, Scheduled for May.
13. Cornelissen, G.; Rigterink, H.; ten Hulscher, D. E. M.; Vrind, B. A.; van Noort, P. C. M. *Environmental Toxicology and Chemistry* 2001, 20, 706–711.

ANNEX 10: OVERVIEW OF STUDIES PERFORMED IN CANADA

Uptake of silver and cadmium in the American plaice and the snow crab¹⁻²⁻³ (inter-species differences)

The fate of silver differs strongly between these two species. In the American plaice, about 9 ± 5 % of the silver ingested with food is assimilated and it is eliminated rather rapidly, with a half-life ($t_{1/2}$) of 48 ± 36 d. In the snow crab, however, assimilation efficiency (AE) was 89 ± 12 % and the elimination was very slow, with a half-life of >1000 d. The efficient uptake and slow elimination of silver in the snow crab may be due to the physiological importance of copper in decapod crustaceans and the chemical kinship of silver and copper. From these results, a long-term uptake model predicted Ag levels snow crabs should be much higher than in the American plaice at given sampling site, a prediction confirmed by field data collected in the Estuary of the St. Lawrence (Québec, Canada). Recent work with other crustaceans showed that silver appears to behave in the same way as in the snow crab (Warnau and Rouleau, unpublished data).

Snow crab assimilates more dietary Cd ($AE = 42 \pm 9$ %) and eliminates it at a slower rate ($t_{1/2} = 199 \pm 36$ d) compared to the American plaice ($AE = 17 \pm 8$ %, $t_{1/2} = 93 \pm 29$ d). Model calculations predicted that under field conditions, snow crab hepatopancreas would have cadmium concentrations 4 to 5 times higher than in the liver of the American plaice. This prediction corresponded well to data collected during a monitoring campaign in the St. Lawrence Estuary.

Tremendous variations can be observed for the concentration of a given metal in different species. Although it may seem obvious for scientists involved in biomonitoring, these variations may be misleading for non-scientists. It must be kept in mind that high concentration values that may represent a real risk for a given animal species can be quite normal for another one.

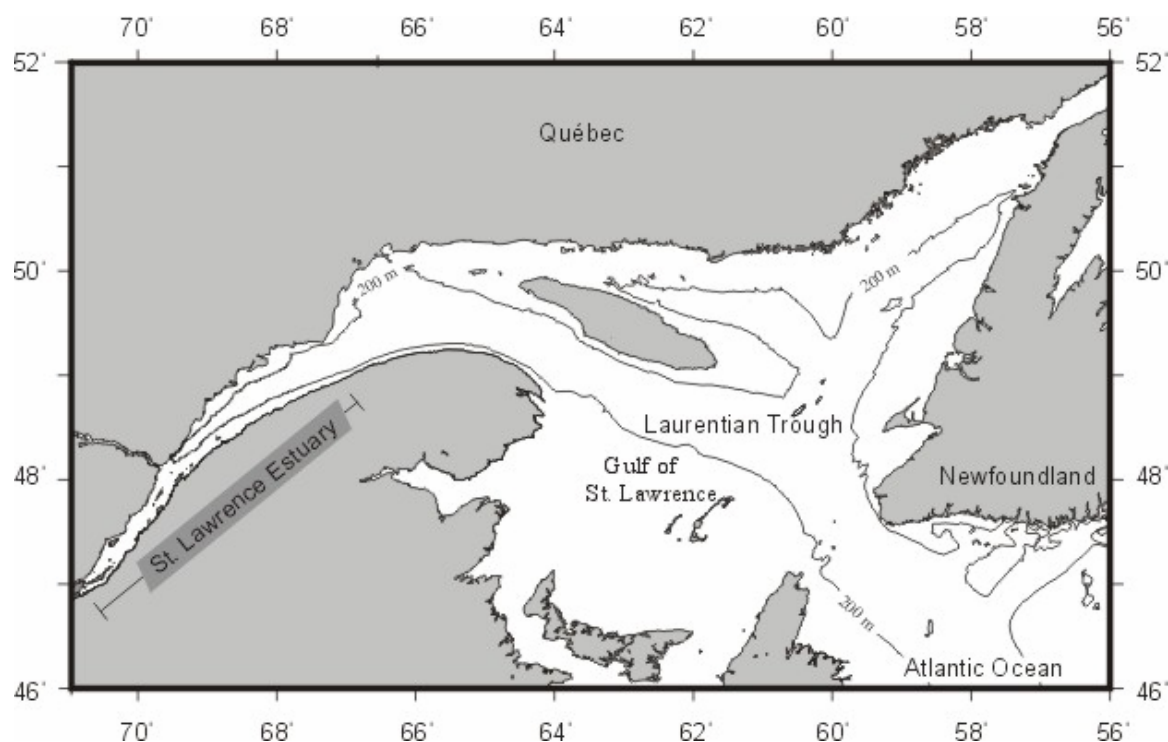


Figure A10.1. The Estuary and the Gulf of the St. Lawrence River in Canada.

Cadmium levels in demersal fish in the Estuary and Gulf of the St. Lawrence³ (influence of diagenetic processes on the trophic transfer of cadmium in the benthic food web)

The Estuary and the Gulf of the St. Lawrence River in Canada are characterised by the presence of a 1200-km long and deep (300–500 m) trough, the Laurentian Trough (see Figure A10.1). Sediment of the Laurentian Trough receives all the contaminants load carried by the St. Lawrence River from the densely populated area of the Great Lakes. As a result, the sediments of the Laurentian Trough exhibit a seaward decreasing gradient of many metallic contaminants, such as silver and mercury, as well as a gradient of pollution by organic compounds, such as PAHs. However, for some

other metals, an important enrichment is seen in the deeper layers of the sediments for elements such as cadmium, uranium, and molybdenum. These profiles may appear at first to be the result of anthropogenic contamination. This phenomenon is due to purely natural diagenetic processes. Hence, concentrations of cadmium in the sediments of the Gulf are higher than those in the Estuary, despite the fact that dissolved Cd concentrations in the deep-water layer of the Laurentian Trough, approximately 0.3 nM, show little variation along its length. Actually, the vertical distribution of Cd in the fine-grained sediments of the Trough is similar, being characterised by a sharp concentration gradient at about 1 cm depth, at the oxygen penetration depth. This is the result of the downward diffusion of dissolved Cd into the sediments and its precipitation as Cd sulphide. Nevertheless, due to the progressive decrease of detrital Cd flux along the Trough, authigenic Cd is less diluted by Cd-poor detrital particles, resulting in Cd concentration in the subsurface that are twice as high in the Gulf compared to the Estuary (see Figure A10.2).

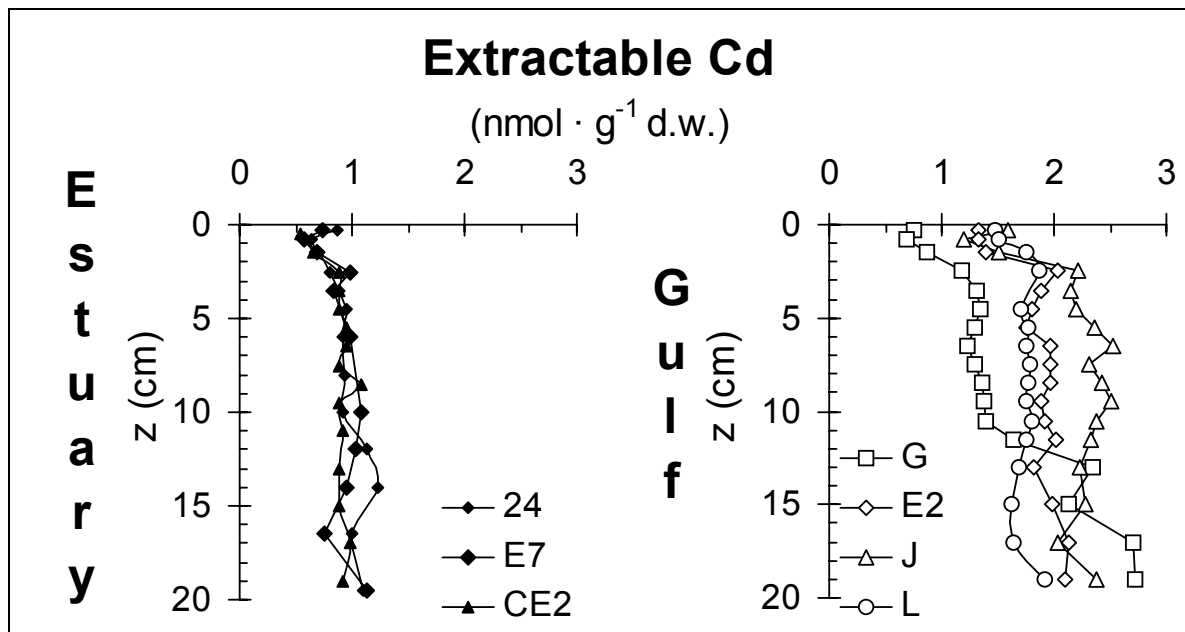


Figure A10.2. For explanation see text.

In order to verify sedimentary cadmium concentration differences due to diagenetic processes that can affect the cadmium levels in benthic predators, hepatic cadmium burden has been measured in 312 demersal fish belonging to four different species: the Atlantic cod (*AC*), Greenland halibut (*GH*), American plaice (*AP*), and thorny skate (*TS*). Results showed that Cd levels in these fish were correlated with the horizontal distribution of Cd levels in the sediments, with values (nmol hepatic Cd / kg body weight) in fish from the Gulf that were at least twice as high compared to fish from the Estuary (*AC*, 155 ± 78 Gulf, 98 ± 43 Estuary; *GH*, 39 ± 27 Gulf, 9 ± 9 Estuary; *AP*, 50 ± 44 Gulf, 26 ± 24 Estuary; *TS*, 190 ± 82 Gulf, 77 ± 44 Estuary)

Seasonal variations of apparent Cd concentration in the liver of the Atlantic cod³ (influence of seasonal physiological variations)

Normal physiological variations occurring during the year may have strong effects on metal concentrations measured and may lead to false conclusions. One example is that in the work mentioned above, it has been found that hepatic cadmium concentration values in the Atlantic cod were higher in fish from the Estuary whereas the hepatic cadmium burden was higher in fish from the Gulf. This discrepancy between concentration and hepatic burden data can be explained by the fact that sampling in the Estuary took place during spring whereas fish from the Gulf were sampled in summer and the beginning of winter.

Hence, the feeding rate of Atlantic cod is high in the summer and through the beginning of the winter, and very low during late winter and spring. Seasonal variations of the feeding rate affect both the size of the liver, which is where cod accumulates most of its energy reserves, and the hepatic Cd content. However, variations of liver size (3 x) are greater than those affecting the hepatic Cd burden (1.5 x). As fish from both the Gulf and the Estuary are submitted to the same seasonal pattern of their feeding rate, the temporal variations of Cd hepatic burden of both cod populations are parallel and the hepatic Cd burden of cod in the Gulf is always higher than that of cod living in the Estuary. This corresponds to the horizontal distribution of sedimentary cadmium concentrations observed in the St. Lawrence. However, cod from the

Estuary were sampled at a time when liver size was minimal, whereas cod from the Gulf were sampled at times when liver size was at its maximum, resulting in an apparent dilution and decrease of hepatic cadmium concentration. It thus appears that hepatic cadmium burden is a more robust comparison tool than hepatic concentration.

Pharmacokinetics of methylmercury and tributyltin in the American plaice and the snow crab⁴⁻⁵ (assessment of biomagnification potential)

Biomagnification of methylmercury in marine food chains is a well-known phenomenon that has resulted in a fish consumption advisory being issued in many countries due to the high levels of this neurotoxic organometal found in top predatory fish. Pharmacokinetics of tributyltin, a highly toxic organometallic compound used in antifouling paints, have been quantified in the American plaice and the snow crab and compared to those of methylmercury in order to evaluate the biomagnification potential. Pharmacokinetic parameters measured were used to model the long-term accumulation of both tributyltin and methylmercury in these two benthic predators. Modelling results showed that the dietary transfer of tributyltin resulted in biomagnification factor values below 1 (≈ 0.1 for the snow crab and ≈ 0.5 for the American plaice), whereas the biomagnification factor of methylmercury was 2 for both species. This is mostly because tributyltin has a much shorter biological half-life compared to MeHg, due to its fast metabolism. It therefore appears that tributyltin is not likely to be biomagnified, though this depends also on the extent of tributyltin accumulation by organisms belonging to lower trophic levels.

1. Rouleau C., Gobeil C., Tjälve H. (2000). Accumulation of silver from the diet in two marine benthic predators: the snow crab (*Chionoecetes opilio*) and the American plaice (*Hippoglossoides platessoides*). Environ. Toxicol. Chem., 19(3): 631–637.
2. Rouleau C., Gobeil C., Tjälve H. (2001). Cadmium accumulation in the snow crab *Chionoecetes opilio*. Mar. Ecol. Prog. Ser., 224: 207–217.
3. Rouleau C., Gobeil C., Tjälve H. (200x). Uptake of cadmium in coastal demersal fish. Limnol. Oceanogr., submitted.
4. Rouleau C., Gobeil C., Tjälve H. (1998). Pharmacokinetics and distribution of dietary tributyltin compared to those of methylmercury in the American plaice (*Hippoglossoides platessoides*). Mar. Ecol. Prog. Ser., 171: 275–284.
5. Rouleau C., Gobeil C., Tjälve H. (1999) Pharmacokinetics and distribution of dietary tributyltin and methylmercury in the snow crab (*Chionoecetes opilio*). Environ. Sci. Technol. 33: 3451–3457.

ANNEX 11: TWO COMPARATIVE STUDIES OF METALS IN GEOGRAPHICALLY DIFFERENT SAMPLES ANALYSED AFTER TOTAL AND PARTIAL DIGESTION

In this annex data are collected on samples for which metals were analysed both after partial as well as total (HF) digestion.

Data set No. 1

Metal analyses in QUASH samples

At WGMS 2002 in San Sebastian, Carla Palma (Inst. Hidrografico), presented results of QUASH samples analysed by partial and total digestion. These were samples that were principally equally polluted but with variable grain size artificially achieved by sieving. The QUASH experiment consisted of 3 individual samples which were sieved:

- estuarine sample from Portugal [17 MS (<2 mm); 18 MS (>63 µm); 19 MS (<63 µm); 20 MS (20–63 µm); 21 MS (<20 µm)]
- marine sample from Portugal [22 MS (<2 mm); 23 MS (>63 µm); 24 MS (<63 µm)]
- reference sample from QUASH [13 MS (>63 µm, sieved by IH); 14 MS (<63 µm, sieved by IH); 15 MS (>63 µm); 16 MS (<63 µm)]

The results obtained for Cd, Hg, Cu, Cr, Mn, Zn, Fe and Pb indicate that there are no obvious differences between total and partial digestion. (Graphs presented at WGMS 2002). For Li and for Ni the partial digest generally produced higher results than the total digest. For Al the total digest show higher results than the partial digest especially for coarse samples.

This digestion of QUASH samples with both methods was repeated in 2003 but now both digests were analysed by AAS (IH) and ICP-MS (RIKZ). For all the elements the results were very similar to previous work and no obvious differences were found between total and partial digestion for Cd, Hg, Cu, Cr, Mn, Zn, Fe and Pb. Mainly for coarse samples partial digestion results in lower values for Al. Like the previous tests for Li and Ni again awkward differences were observed. For those elements the results are presented in Figure A11.1. For Ni a slight tendency to higher results was observed for partial compared to total digests when analysed by AA and sometimes when analysed by ICP-MS. For Li partial digest generally produced higher results than the total digest with AA and ICP-MS.

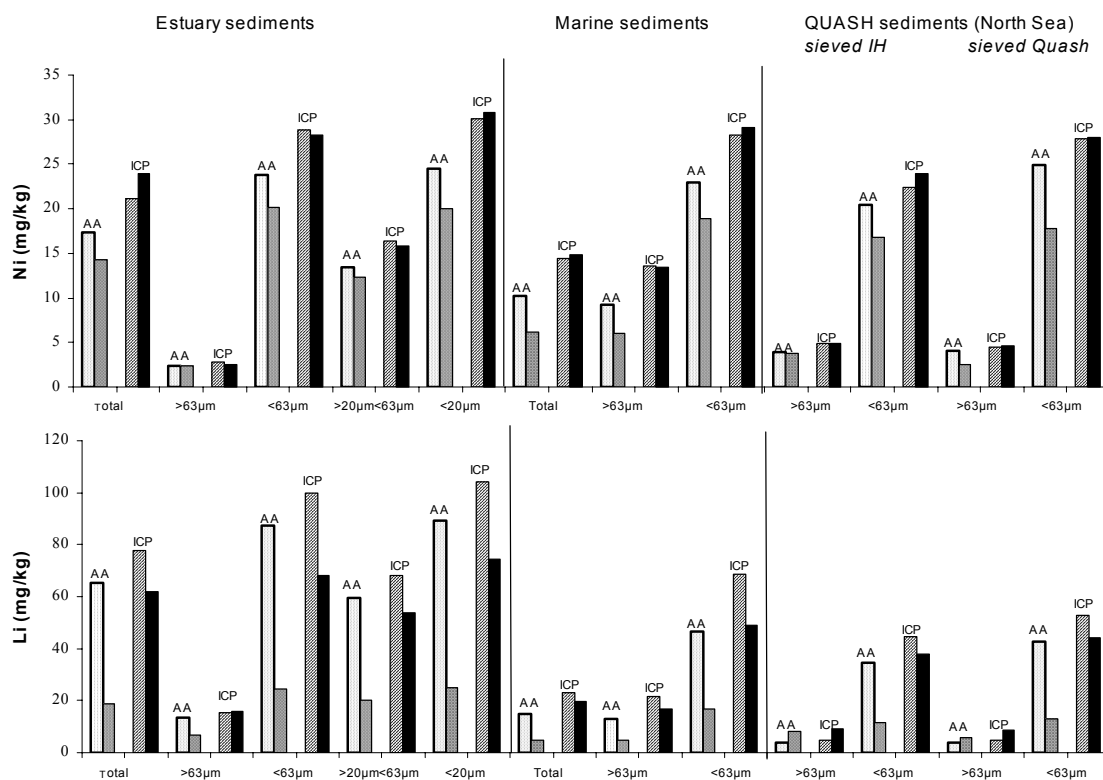


Figure A11.1. Ni and Li contents in QUASH sediment samples from Portugal and North Sea measured by AA and ICP-MS after partial and total digestion.

Data set No. 2

Comparison Studies undertaken by RIKZ and Warnemünde

In the graphs below (Figures A11.2–A11.7) the results of analyses of samples from the DIFFCHEM project are given. This included samples from Otrå in Norway, Elbe in Germany, Oyster grounds in the North Sea, Mersey in United Kingdom and Seine in France. In addition samples from Ems Dollard were available and analysed using the same procedures. These samples from the different geographical locations were separated in fractions with different grain size composition by sieving and sometimes sedimentation. After sieving the samples were freeze-dried and homogenised by a ball mill. Sub samples were analysed for the clay content by “pipette-method”.

Other sub-samples were analysed for heavy metals by strong partial digestion and total digestion. The partial digestion was performed at RIKZ by using 5 ml concentrated Nitric acid 1:1 diluted with water. The mixture was heated for 16 hours in a pressure vessel at 140°C. After cooling the sample was transferred to a 200 ml volumetric flask. Metals were analysed in the digest by ICP-OES. Other sub-samples were analysed by the Baltic Sea Research Institute in Warnemünde, Germany using total digestion including HF. The results are presented in the graphs below (Figures A11.2–A11.7). All metals are expressed in mg/kg except that Al, Ca, Fe, K and Mn were in g/kg. On the x-axis the clay content is expressed in %. The data were plotted versus the clay content (x-axis), to show the differences or similarities between total and partial digestion in relation to the physical sample composition measured in the samples.

The results show that it is not obvious that a total digestion gives higher results. In many cases the data from the partial digestion were higher and for the finer fractions almost always. In a number of cases the higher values for the total digestion are very well explainable as for example aluminium in the Otrå in Norway. The coarse material is most likely dominated by feldspar known to be commonly present in North Atlantic sediments. At other locations also the coarse material may contain some feldspar or other aluminium-containing minerals. In the samples (fractions) where the coarse material is absent total and partial methods do not significantly differ for elements like Al and K.

Differences between methods for Li are not evident in this data set. Li is systematically higher for partial digestion but not very abundant. A comparison of digestion methods gives remarkable results for Ni. For Oyster grounds and Elbe Ni contents are quite the same while for other areas there are large differences comparable with those found in the QUASH samples.

Although partial digestion generally results in higher contents, because differences are not systematic and vary with locations it is not likely that this can be caused by the instrumental measurement after digestion. Therefore it seems that the variable composition of the matrix influences the instrumental measurement. A lower matrix is expected for partial digestion which could lead to lower suppression of the signal. However due to lack of information on matrix influences no firm conclusion can be drawn. Nevertheless the set belief that partial methods will result in lower concentrations is not supported by the observed results.

Further interpretation of the data would be required to evaluate the meaning of this outcome for the application of the present normalisation guidelines. It is clear that in the application of Al as normaliser the pivot points will differ a lot between using a total or partial method. The data maybe also allow investigation of which parameter is a better representative for the clay content: Al using a partial or using a total digestion method?

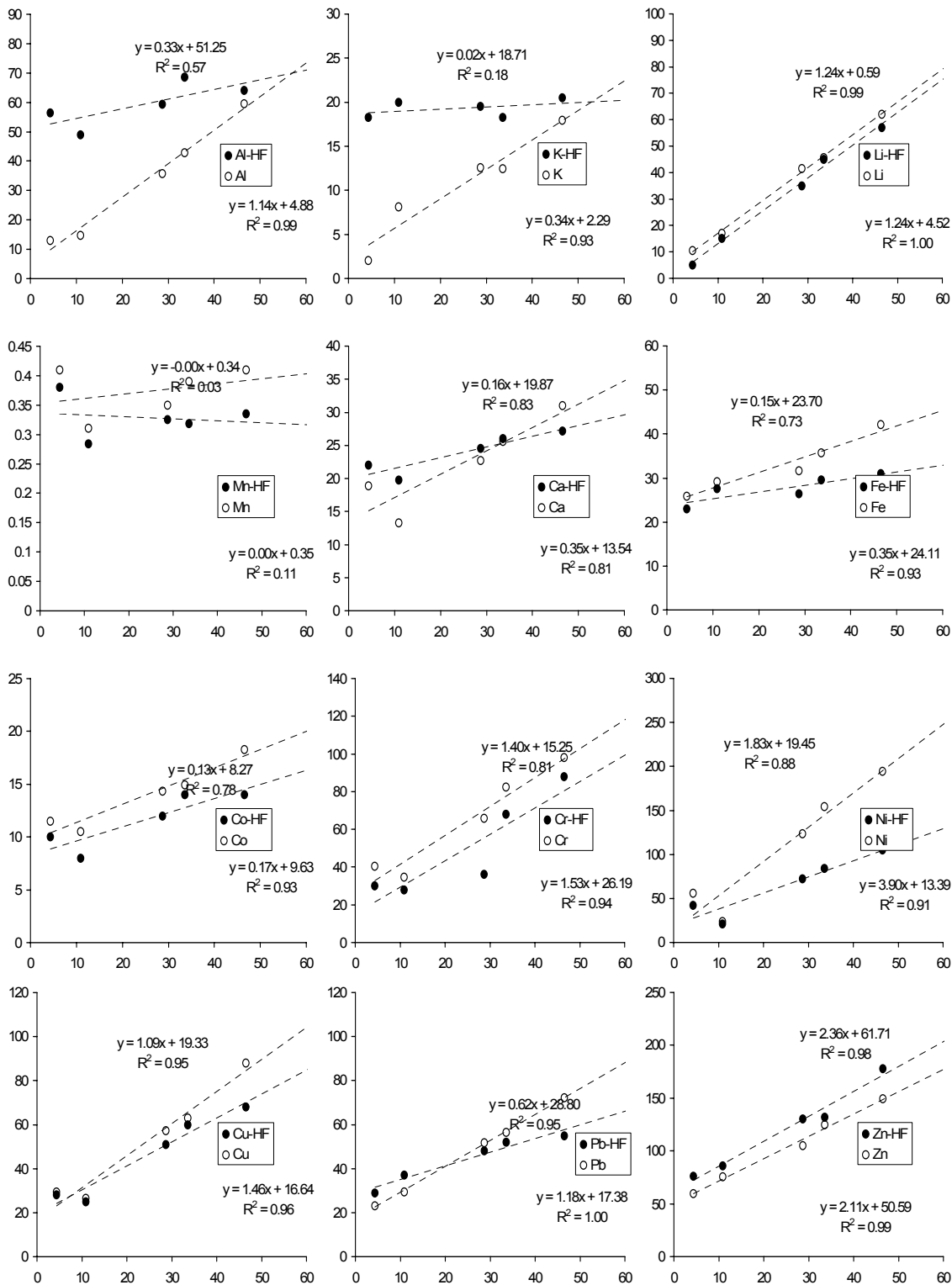


Figure A11.2. OTRA-Norway (for explanation see text).

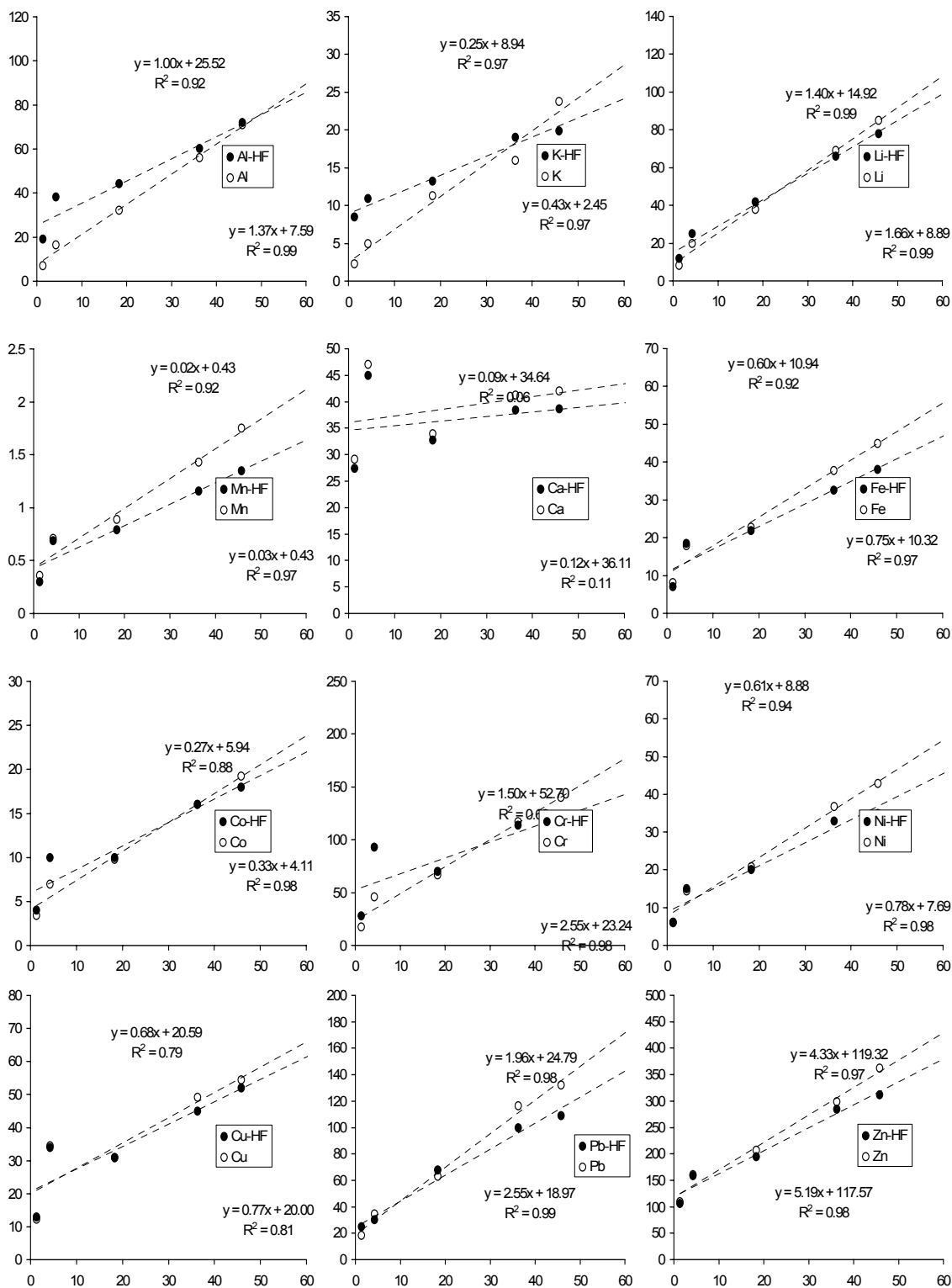


Figure A11.3. Mersey UK (for explanation see text).

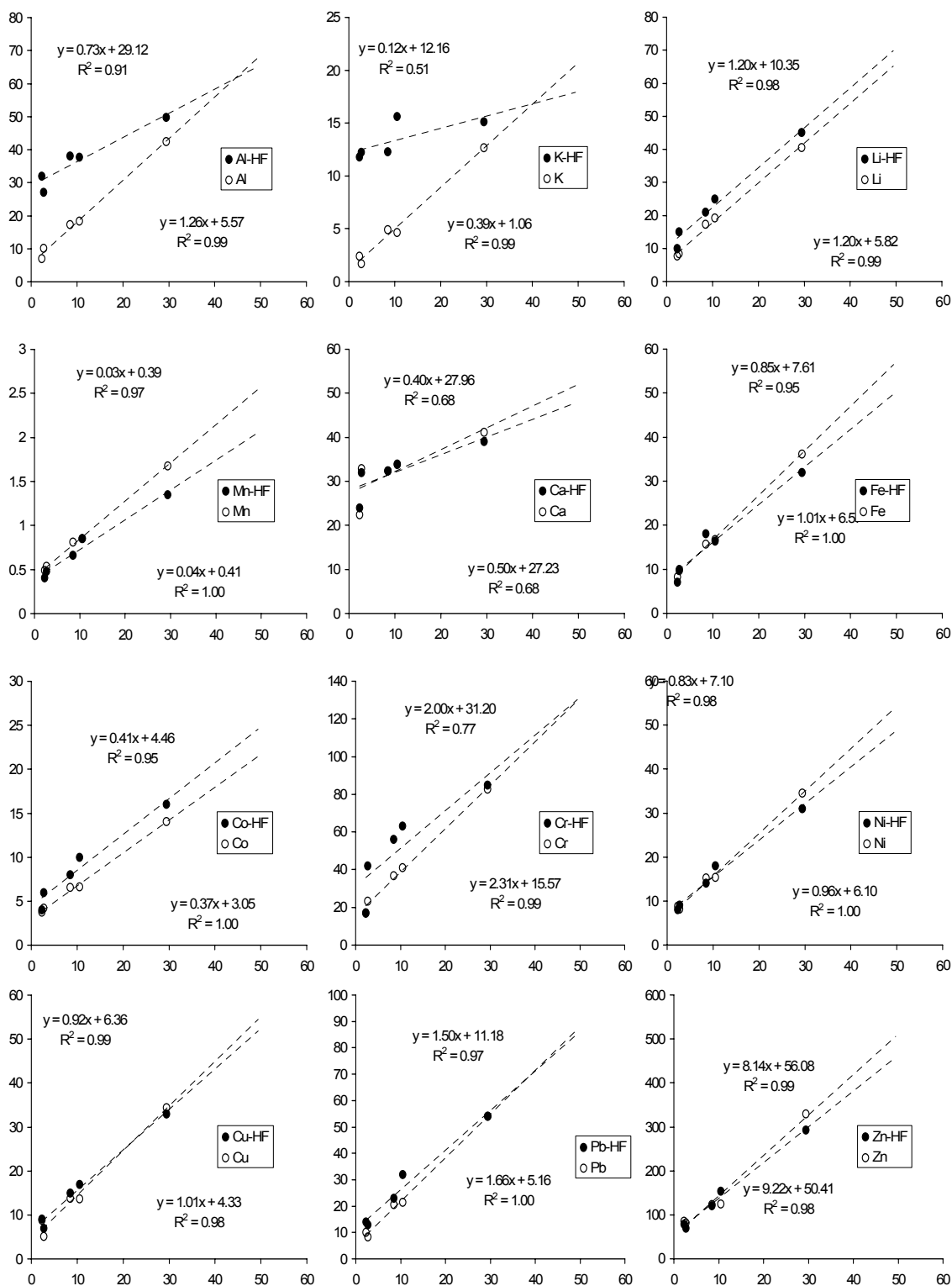


Figure A11.4. Elbe D (for explanation see text).

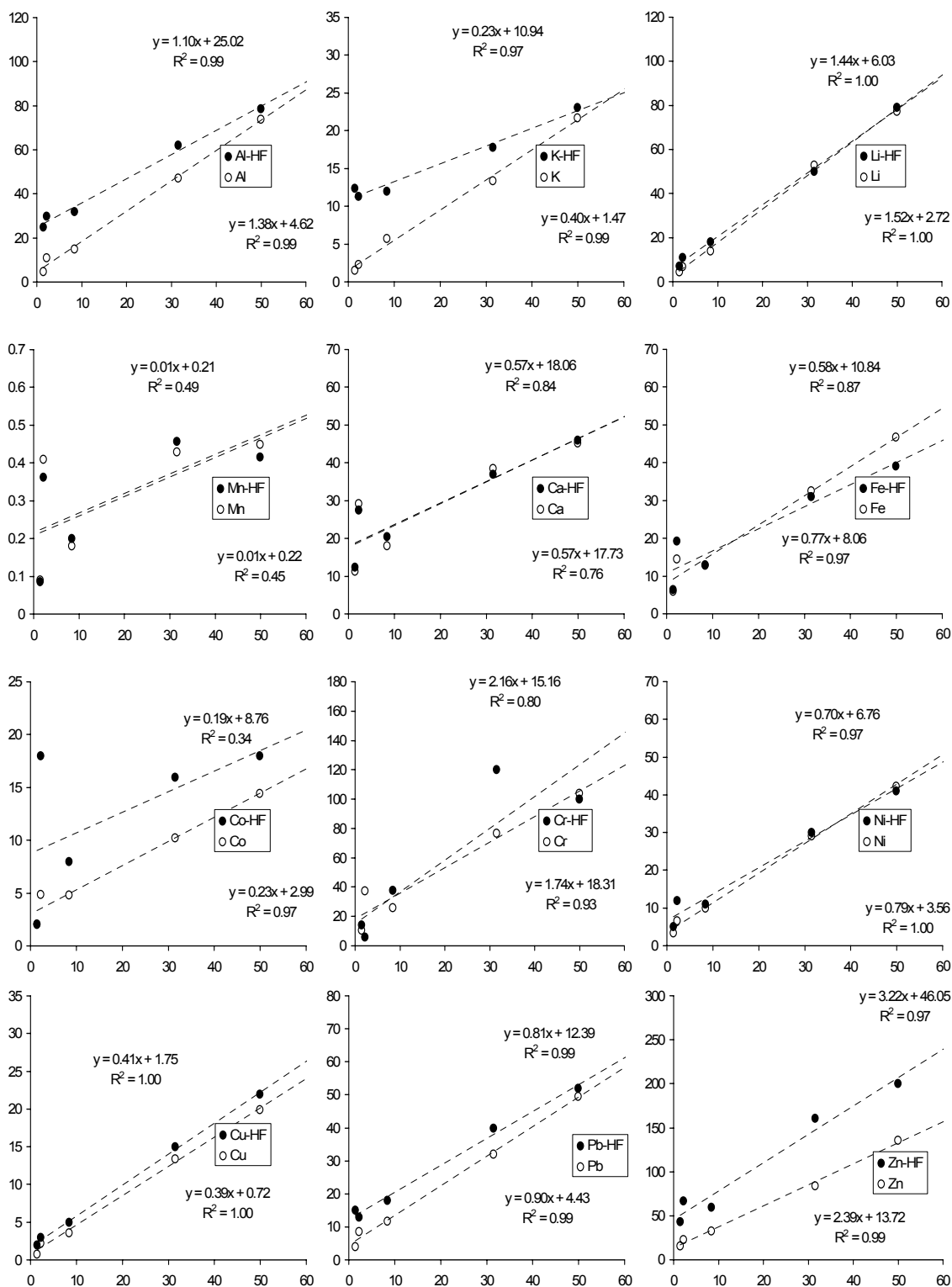


Figure A11.5. Oyster grounds North Sea (for explanation see text).

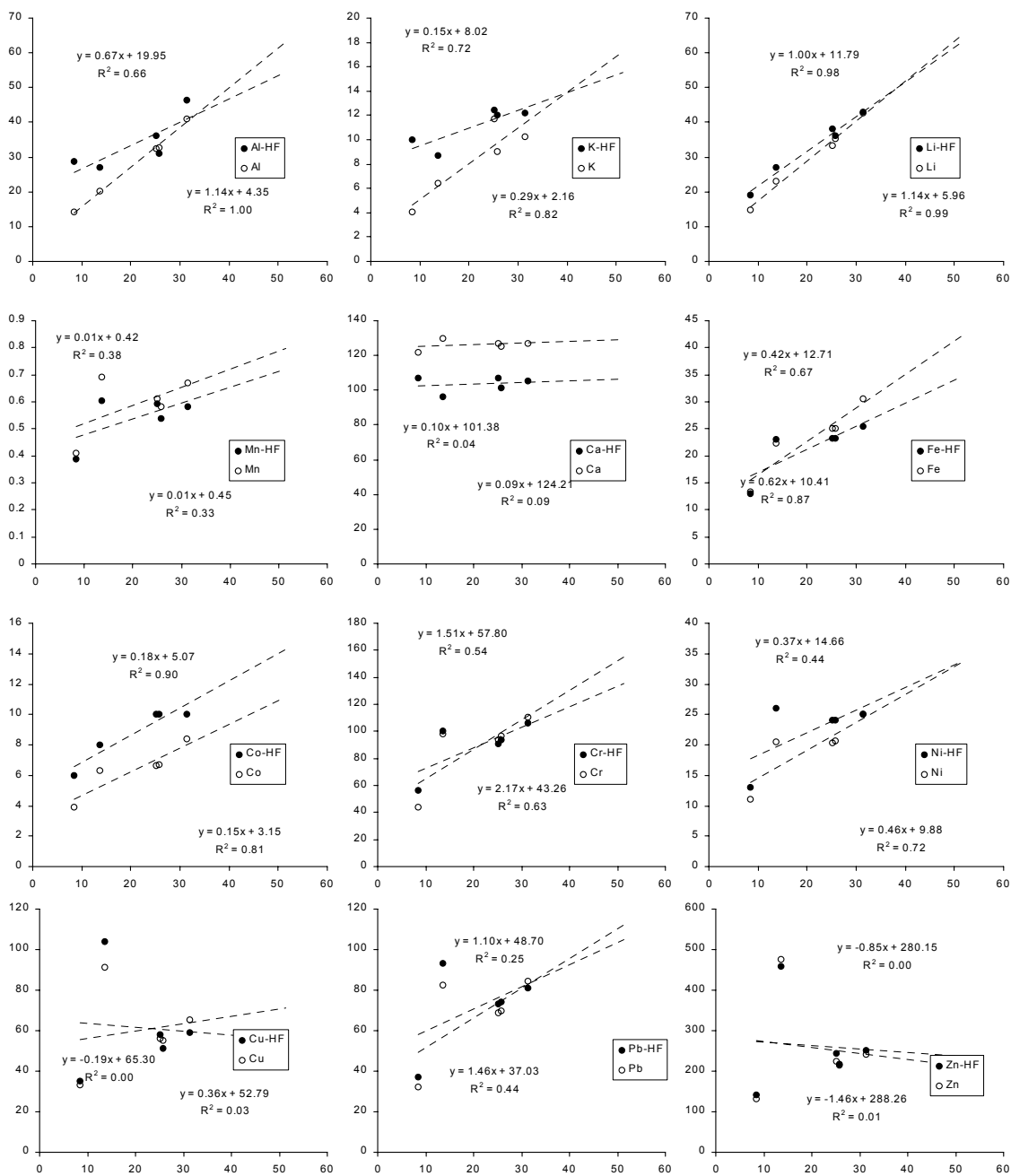


Figure A11. 6. Seine (for explanation see text).

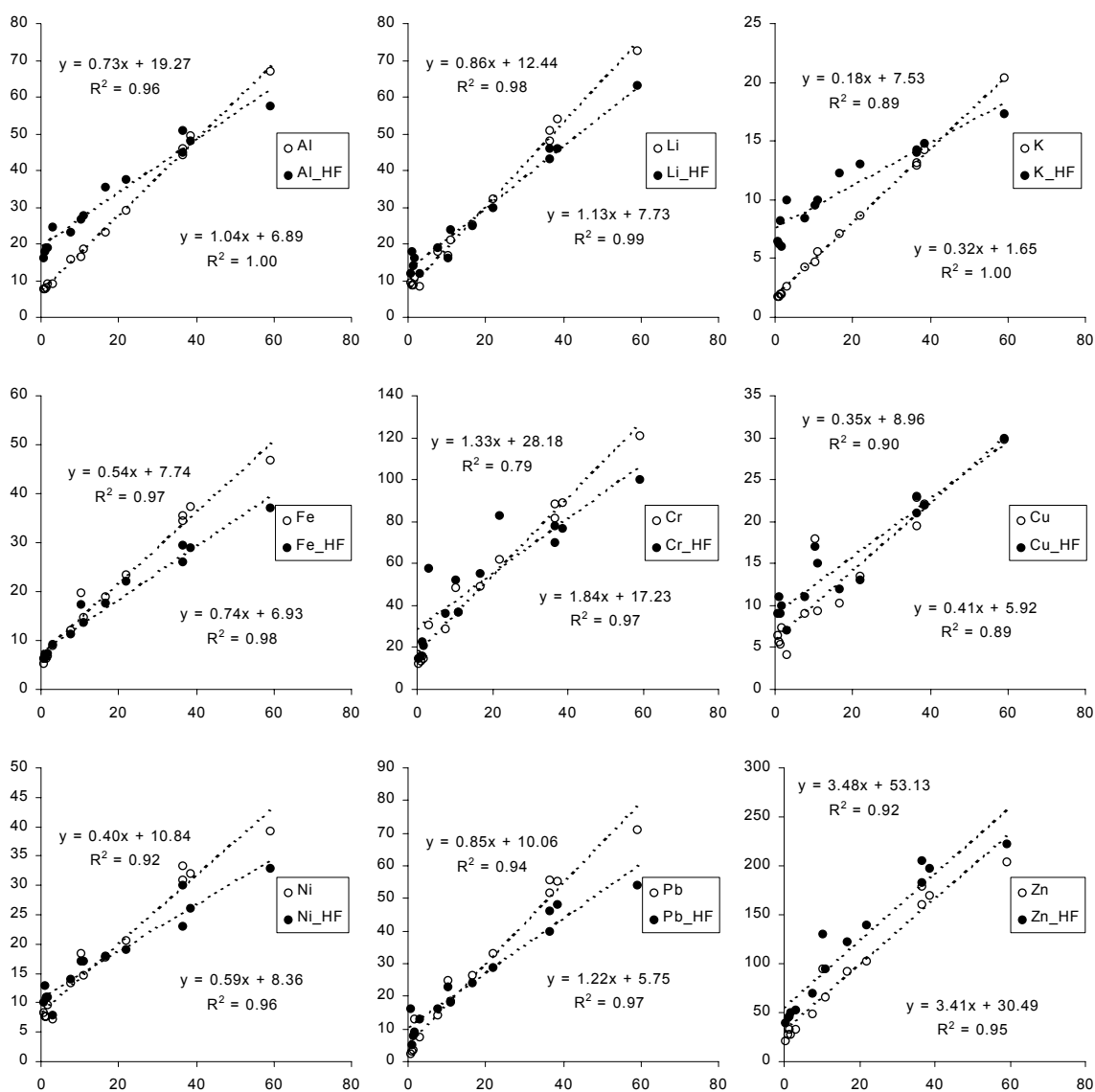


Figure A11.7. Ems Dollard (for explanation see text).

ANNEX 12: RECOMMENDATIONS

The WGMS recommends that:

1. the Inventory of Sediment Quality Criteria, after review and adoption by ACME, be forwarded to OSPAR MON and HELCOM MONAS for use in their assessments of sediment quality and to EEA and SEDNET for information.
2. the working document on sediment dynamics in relation to sediment trend monitoring be forwarded informally to OSPAR MON and HELCOM MONAS for information and to receive their comments.
3. the inventory on national sediment temporal trend monitoring, after review and adoption by ACME, be forwarded to OSPAR MON and HELCOM MONAS for use in their assessments.
4. work continue on the measurement of potential (bio)available concentrations in sediment and include metals with the aim of making a document available after next year's meeting.

The **Working Group on Marine Sediments in Relation to Pollution** [WGMS] (Chair: F. Smedes, Netherlands) will meet from 1–5 March 2004 in Stockholm, Sweden to:

- a) continue the work on the measurement of the potential bioavailability of contaminants in sediment and evaluate the work done in the Western Scheldt intersessionally done by Belgium and the Netherlands;
- b) finalize work on the annex to the sediment monitoring guidelines that provides guidance on the interpretation of sediment trend monitoring data, taking into account sediment dynamics;
- c) continue work on the development of indicators of sediment contamination;
- d) further investigate the possibilities of integrated chemical and biological effect monitoring and evaluate where the knowledge on chemical sediment monitoring can contribute to application and interpretation of biological effects monitoring (with WGBEC);
- e) investigate the possibilities and present use of suspended matter for monitoring programmes.

WGMS will report by 22 March 2004 for the attention of the Marine Habitat Committee and ACME.

Supporting information

Priority:	This group handles key issues regarding monitoring and assessment of contaminants in sediments.
Scientific Justification:	a) Present monitoring methods are based on measuring the total contaminant concentrations in sediments. The resulting data do not necessarily represent the environmental risk, due to the limited bioavailability of many contaminants in sediments. WGMS is an appropriate platform to discuss and investigate alternative methodologies for sediment assessments for future advice to ICES on taking bioavailability into account. b) The proposed annex to the Sediment Monitoring Guidelines is an essential addition that will assist ICES in providing advice to others, e.g., OSPAR and HELCOM, on the interpretation of monitoring data with a view to detecting temporal changes in sediment quality. For this, sediment dynamics are of great importance as they affect the evolution of all sediments and a description of their influence should be included in the proposed Annex. c) Although the progress on this point is limited, development of practical indicators for sediment quality is of paramount importance to display the results of environmental assessments to the general public. Therefore the group should continue to develop such indicators and, where possible, demonstrate and evaluate some presently applied procedures. d) Discussion on the integration of sediment and biological effects monitoring did not come much further than taking samples at the same place and time. Especially biological effects monitoring techniques that include sample preparation, extraction and separations may benefit from evaluation by the WGMS. Perhaps through this route integrated guidelines can be developed. This is useful for both biological effects and chemical monitoring, to support interpretation and provide better assessment of the marine environment. e) Several countries (e.g., Germany, The Netherlands) collect suspended matter in or outside monitoring programmes. The potential of monitoring this future or past sediment in relation to sediment monitoring is unknown. An inventory of such programmes and evaluation of

	the existing results may reveal some of the above aspects.
Relation to Strategic Plan:	
Resource Requirements:	None required
Participants:	Subjects like bioavailability and sediment quality criteria (SQC) are of mutual interest to both WGBEC and WGMS. Periodic interactions between the groups and transfer of information are essential for efficient operation of both groups. Selected and interested members of the WGMS should participate in work of the WGBEC for the interaction and information transfer on the mutual issues such as SQC and bioavailability.
Secretariat Facilities:	None required
Financial:	None
Linkages to Advisory Committees:	ACME
Linkages to other Committees or Groups:	WGBEC, MCWG
Linkages to other Organisations:	OSPAR, HELCOM
Cost share	ICES 100 %

ANNEX 13: ACTION LIST

1. Kristoffer Næs will collect information on the use of DGT in Norway.
2. Maria Jesus Belzunce and Kristoffer Næs will collect information on integrated monitoring approaches.
3. Claude Rouleau, Jean-Louis Gonzalez, Patrick Roose and Hanneke Gieske will contribute with information on sediment dynamics for other areas such as the St. Lawrence Gulf and Estuary, the Bay of Biscay and the Scheldt estuary.
4. Foppe Smedes and Patrick Roose will report the outcome of a study on the availability of HOCs in sediments from the Scheldt estuary.