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Exploration of the Sea

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

Savannah, Georgia, USA
20-23 February 1989

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

Skidaway Institute of Oceanography
Savannah, Georgia, USA
20 - 23 February 1989

1 OPENING OF MEETING AND ADOPTION OF AGENDA

The meeting was opened by the Acting Chairman, John Calder, at 9.00 hrs on 20 February. The WG was welcomed to Skidaway Institute by Herb Windom. Herb also introduced Dannah McCauley who would provide for our copying and typing needs. Following a brief introductory statement by each attendee, the WG embarked on the agenda. The final agenda appears as Annex 1 to this report and the list of participants as Annex 2. A list of abbreviations and acronyms used in this report appears as Annex 3.

2 REPORTS ON ACTIVITIES OF INTEREST TO THE WORKING GROUP

2.1 Results of 76th Statutory Meeting

A brief summary of activities from the 76th Statutory Meeting of relevance to the WG had been submitted by the ICES Environment Officer. These activities in essence determined the agenda for most of this WG meeting.

2.2 Other ICES Working Groups

2.2.1 Marine Chemistry Working Group (MCWG)

The Chairman briefly reviewed the activities of the MCWG meeting of the previous week and drafts of MCWG sub-group reports were made available for information purposes. The Chairman of WGEAMS, who is also a member of MCWG, asked WGMS to comment on the matrix tables prepared by WGEAMS and expanded on by MCWG. The Chairman noted that the organics sub-group of MCWG had not completed its review of the matrix tables, which accounted for the absence of many organic contaminants from the tables. The WGMS concluded that it did not wish to pursue the filling-in of boxes in the matrix table for fear that others might read such a table as a requirement for all monitoring programs. The WG wishes to work with WGEAMS in this regard, but feels that a better context for the matrix tables is required.

2.2.2 Working Group on the Biological Effects of Contaminants (WGBEC)

The Chairman briefly summarized the plan for a biological effects workshop to be conducted by the WGBEC. Information available to the Chairman indicated that the place (Bremerhaven, Federal Republic of Germany) and time (April, 1990) had been defined, but that scientific specifics were still under discussion. The Chairman informed the group that the MCWG had been asked to comment on the workshop from a chemical perspective, but had declined to do so given the limited specific information available on the workshop. It seems probable that there will be a significant number of sediment-based studies at the workshop, but given the timing, the WGMS will have no opportunity to provide input.

2.2.3 Working Group on the Statistical Aspects of Trend Monitoring (WGSATM)

The Chairman introduced Annex 5 from the 1988 WGSATM report which formed the basis for one of the terms of reference for this meeting of the WGMS. At the request of the Chairman of WGSATM, the WGMS will review a paper by Uthe et al. (Sampling Strategies for Trend Monitoring Using Biota, Sediments and Seawater) that will be submitted to the next meeting of WGSATM. The WGMS will consider the need for additional guidelines for the use of sediments in trend monitoring of contaminants.

2.2.4 Working Group on Environmental Assessments and Monitoring Strategies (WGEAMS)

The matrix tables, drafted by WGEAMS and expanded by MCWG, are discussed in Section 2.2.1, above.

2.2.5 Advisory Committee on Marine Pollution (ACMP)

The Chairman made available relevant sections of the 1988 report of ACMP (Cooperative Research Report No. 160). The contents of the report defined a large portion of the remaining agenda.

2.3 Joint Monitoring Group (JMG) of the Oslo and Paris Commissions and the Standing Advisory Committee for Scientific Advice (SACSA) of the Oslo Commission

The ICES Environment Officer had distributed a summary of the 1988 SACSA meeting. Normalization had been considered by SACSA, but no firm conclusions were reached pending advice from ACMP. Leendert van Geldermalsen stated that the paper he will present under agenda item 6.3 has also been presented to SACSA.

With regard to JMG, the WG was informed by Jens Skei and Tereza Vinhas that a collection of sediments is to be conducted in 1990 under the auspices of the Joint Monitoring Programme (JMP). They felt that the report of this meeting of WGMS could be very helpful to JMG in completing the plans for that activity.

2.4 Intergovernmental Oceanographic Commission (IOC)

Herb Windom reported on the sediment workshop being planned by the Group of Experts on Methods, Standards and Intercalibration (GEMSI). The Workshop will take place in Dalian, China, for two weeks in September, 1989. The purpose is to assist IOC in developing a monitoring approach for use in various regional areas and to provide training for laboratories from the IOC-Westpac region. Dalian Bay has a known gradient of contamination and strong local support is available from the Institute for Marine Environmental Protection at Dalian. About 30 participants are expected, half from China. Coordinators of the workshop are Herb Windom, Doug

Loring, Manfred Ehrhardt and Rodger Dawson. Both trace elements and trace organic contaminants will be considered. During the workshop, surface sediment samples will be collected over the contamination gradient; cores will also be collected. Doug Loring added that the coordinators had collected samples during a visit to the site in January, 1989. These will be analyzed prior to the workshop by the coordinators to confirm sampling sites. Also, the coordinators will distribute to the participants sub-samples of a known material for intercomparison purposes.

The Chairman reported that the IOC Group of Experts on Standards and Reference Materials (GESRM) has not met again since its first meeting in the summer of 1987. He also noted that some consideration is being given to the inclusion of sediments in the proposed International Mussel Watch Programme being planned under both IOC and UNEP auspices.

2.5 Other Relevant Activities

The Chairman invited members to prepare brief written statements regarding national activities that would be of interest, other than those already on the agenda. No written material was prepared during the meeting.

3 APPROACHES TO NORMALIZATION OF TRACE METAL CONCENTRATIONS IN SEDIMENTS

3.1 Guidelines Document

The Chairman initiated the discussion by reviewing the ACMP comments on the "Guidelines for the Normalization of Trace Metals in Sediments" included as Annex 4 to last year's WGMS report. He stated that ACMP took no issue with the substance of the report, only the style. It was agreed by the WG that the document could be rewritten to emphasize the most common approach to normalization while identifying those circumstances in which the approach might not be effective. The Chairman introduced a revised version of the guidelines document that had been prepared by the former WGMS Chairman, Roland Wollast, and also a letter from John Portmann, Chairman of ACMP, that provided additional clarification of the charge to the WGMS. The Chairman then appointed Herb Windom and Doug Loring to prepare a revised draft of the guidelines for the WG to consider.

There was considerable discussion over the meaning of the word "normalization" and when it should be used. All members of the WG agreed on a definition and on the need for the guidelines document to include this definition. Briefly, "normalization" will be viewed by the WG to mean the attempt to eliminate the variability occurring from natural processes controlling background levels of substances that have both a natural and an anthropogenic source. Thus, normalization can be used to attempt to distinguish the anthropogenic from the natural trace metal content of sediments. The concept of normalization as defined here does not apply to substances that do not have a natural, as well as an anthropogenic source, e.g. chlorinated hydrocarbons.

The revised guidelines document appears as Annex 4 to this report. The WG concurred that it should be published by ICES, perhaps in the Techniques in Marine Environmental Sciences series. Due to the limited availability of one of the references cited in Annex 4, FLA-DER (Florida Department of Environmental Regulation) (1988), it is included as Annex 5 to this report.

For those contaminants for which a normalization procedure is not appropriate, the WG recognized that, for comparison purposes, the concentration of a contaminant in the whole sediment may have to be expressed relative to another variable, e.g., % less-than-63 micron fraction or % total organic carbon. In this way, large changes in the major components of a sediment may be compensated for. For example, the concentration of a chlorobiphenyl congener in a mostly muddy sediment cannot be compared meaningfully with the concentration in a mostly sandy sediment. However, if both concentrations in the total sediment are divided by the % <63 µm in each sediment, the results are more directly comparable. The process of compensation has been used in the United States to create a better comparison of organic contaminant residues in sediments collected from diverse environments. The same approach might be very useful in comparing data from the JMG area, for example. Tom O'Connor cautioned, however, that this approach becomes less reliable when the % <63 µm fraction is low, because the errors associated with the underlying assumptions become a dominant factor. When applying this approach, he in fact did not use sediments containing less than 20% of material in the <63 µm fraction.

3.2 Normalization of Contaminants to Organic Matter

Ingemar Cato introduced his paper "Normalization of heavy metal data by the gradient method", which was an expansion of a presentation given last year. The gradient method involves a plot of metal *vs*. organic carbon concentration in sediment collected from various regions and the determination of a regression line for the data from each area (see Figure 6 from Cato's paper, included as Annex 6). The slope of the regression line is used to determine whether an area is uncontaminated or is contaminated to varying degrees. Cato concluded that the approach appears to give reasonable results when applied to several areas in Sweden receiving a variety of domestic and industrial wastes. The applicability of this approach to other areas must be tested. It was pointed out that in the study areas in Sweden, not only the metals, but also the organic carbon, were being added as contaminants, with an organic carbon content in sediment of up to 10% reported in the included data. For determining the degree of metal contamination, it was suggested by the WG that plotting metal *versus* lithium might prove more quantitatively informative. Tom O'Connor noted that in the U.S. program attempts to relate metal and organic contaminant content to organic carbon content were unsuccessful because the organic carbon was generally very low and that this attempt actually increased the variance in the data. He found it more useful to relate contaminant content to % fines, since doing so tended to reduce the variance in his data.

4 INTERCOMPARISON EXERCISE ON ANALYSIS OF TRACE METALS IN SPM

Jens Skei stated that no communication had taken place among the three planning coordinators (L. Brügmann, van Geldermalsen and Skei) of this intercomparison exercise since the last meeting of the WGMS. He agreed with the assessment of ACMP that plans for an intercomparison to test analytical aspects regarding trace metals in SPM were well enough developed to proceed, but that plans for a shipboard intercomparison of SPM collection techniques needed more thought. Discussion in the WG resulted in a decision to modify slightly the protocol for the laboratory-based intercomparison exercise presented in last year's report. Testing of a laboratory's ability to perform the filtration step without introducing contamination and to accurately weigh the filters will be deferred to a second phase, after first evaluating each laboratory's ability to accurately and precisely analyze small samples for trace metals.

Jens Skei and Leendert van Geldermalsen were appointed by the Chairman to draft a revised protocol and timetable. These were reviewed and accepted by the WG and appear as Annex 7 to the report. Jens Skei agreed to coordinate this first phase of the intercomparison exercise. The protocol will be submitted to the WGSATM for comment before the exercise is initiated, with the aim of eliciting assistance in statistical analysis of the data returned.

5 STATISTICAL ASPECTS OF CONTAMINANT MONITORING IN SEDIMENTS

5.1 Consideration of Responses from WGSATM

The Chairman introduced Annex 5 from the report of the 1988 meeting of WGSATM, which was prepared in response to questions posed by WGMS. WGMS had asked how to determine how many replicates are necessary for various monitoring purposes. The response took the form of an analysis of selected results from the First ICES Intercomparison Exercise on Trace Metals in Marine Sediments (1/TM/MS). While the analysis of the data was done in a very complex way, the conclusions were simple, namely, that the intercomparison of data among laboratories or within a laboratory over time cannot be done without more information. The additional information required from the laboratories is evidence of laboratory stability over long periods of time, usually derived from control charts. Also needed is information on the variance associated with replicate analyses of actual field samples. Members of WGMS agreed to provide this type of information to WGSATM. The WG felt that further analyses of data, as done in the referenced Annex 5, is best done by statisticians, not geochemists, and hoped that WGSATM, with the new information to be supplied by WGMS, would continue these efforts.

5.2 Analytical Precision

Continuing the discussion begun above, several WG members offered to provide data on long-term analytical stability and variance associated with replicate analyses. Herb Windom presented data from his laboratory as an example. These data demonstrated the degree of consistency achieved in his laboratory for analysis of a certified reference material over a multi-year period. He stated that data on replicate field samples collected over a multi-year period were available as well and indicated that they could be made available soon after the meeting. Several other WG members indicated that similar data were probably available in their laboratories. As this is the information that WGSATM appears to need, the Chairman agreed to submit these data to the Chairman of WGSATM before its next meeting, if the data could be made available by the end of March 1989.

6 CONTAMINATION OF SEDIMENTS

6.1 Sediment Hot Spots and the Release of Contaminants from highly contaminated Sediments

Jens Skei presented a paper on hot spot sediments and their environmental significance. Many older industrial facilities are burdened with problems of pollution. As a consequence, the backyard of some industrial companies may be defined as pollution hot spots. Excessive amounts of metals and chlorinated hydrocarbons in the sediments impose a potential environmental risk. It is important to make quantitative assessments of the sediments as a source of pollution. The Norwegian Institute for Water Research has run two experiments on hot spot sediments in a continuous flow system to measure flux rates from the sediments. Additionally, bioavailability tests using fish (eel) and mussels have been done in connection with the flux experiments. The experimental design seems appropriate for the objectives of the studies. The following results can be stated:

i) The release rates of metals and chlorinated compounds are low unless the polluted sediment is resuspended.

ii) Pollutants released from the sediments are rapidly accumulated in mussels and fish.

iii) Eel in physical contact with sediments polluted with hexachlorobenzene showed a high uptake rate.

iv) The level of mercury in fish seems to be controlled by the availability of methyl mercury. The rate of methylation increases with increasing water temperature.

Steve Rowlatt described studies of Liverpool Bay which defined two mud patches near the mouth of the River Mersey where mercury concentrations reached levels of around 2 ppm. Experiments using a model system had been carried out to examine the release of mercury during resuspension of the mud and also during the dumping of dredged material in the bay.

In these experiments, mercury was released in a pulse immediately on resuspension or dumping and then readsorbed within the next few minutes. The release/readsorption cycle allowed the separation of mercury from the particulate matter and its transport away from the resuspension or dumping zone.

Discussion followed on the study of resuspension in the field. As resuspension would occur irregularly and generally during storms, it would not be simple to take measurements to obtain an overall picture of the release of contaminants. Herb Windom suggested the use of caged mussels as the first stage of an assessment of release. This was generally agreed to be a good technique.

6.2 Comparison of Contaminant Concentrations in Sediments and Bivalves from the same Location

Tom O'Connor introduced information from the U.S. that relates to the subject of contaminants in sediment. He reported that in the United States, the National Oceanic and Atmospheric Administration (NOAA) has been conducting its National Status and Trends (NS&T) Program since 1984. A major goal of that program is to monitor spatial and temporal trends of contaminant levels in the coastal and estuarine United States. Reports were distributed to the WG that list the approximately 200 sites sampled in the program and contaminant levels in surficial sediments, mussels, oysters and fish livers. The NS&T data were discussed relative to two distinct issues: compensation of contaminant levels in sediments for the effects of grain size and concordance between contaminant levels in sediments and those in bivalves.

Compensation for Grain Size Differences

The primary reason for not simply reporting the average levels of contaminants in sediments at each of the 200 NS&T sites is that sites dominated by sands would appear to be relatively clean while, in fact, they may be in areas receiving relatively large amounts of contamination. A secondary reason was to account for variations in the fine-grained content of sediments and the influence of that variation on contaminant levels.

The procedure used was to divide all raw data (trace elements and organic contaminants as well) by the fraction of total sediment which was <63 μm in size. Prior to that, however, and more importantly, all sediment samples containing more than 80% sand were excluded from further consideration. Very sandy sediments were simply put into a separate category and data from them were not used when comparing among the 200 NS&T sites. The underlying assumption to this method of compensation is that all contaminants are associated with fine-grained material and that sand only serves to dilute a sediment sample.

It was shown that the variance in the ratio of concentrations measured at each site in each of two years was decreased for all contaminants when the grain size compensation approach was used.

Two alternative parameters were used in an attempt to reduce variance in the data: aluminum (Al) and total organic carbon (TOC). Use of aluminum yielded the same benefits as that of grain-size compensation but, again, it was necessary to disregard samples in the lowest 20% of the range of Al concentrations. That meant not using data from samples containing less than 2% (dry wt) Al.

Use of organic carbon was not helpful. The distribution of TOC is like that of contaminants themselves in that it is log-normal and almost 60% of the TOC values were less than 1% (dry wt) and fell in the lowest 20% of the overall distribution. Without the ability to disregard these low values (and therefore not using 60% of the data), the procedure of dividing all concentrations by TOC increased the variability in the data.

Concordance of Bivalves with Sediments

Reports from the NS&T Program have defined the spatial distribution of contamination in sediments and, separately, in bivalves. There have been 117 sites from which both bivalves and fine-grained sediments have been analyzed. Those data were used to address the question of whether two studies, one using sediments and the other bivalves, would find the same relative ranking of contaminant levels.

Since it was shown that, at a single site, mussels and oysters show very different levels of metal contamination (especially for Ag, Cu, and Zn), it was necessary to consider mussels and oysters separately. Also, to avoid having apparent concordances being dominated by agreement at the most contaminated sites, urban sites (>100,000 people within 20 km) were considered separately from rural sites.

The results were that mussels and sediments do simultaneously reflect high and low levels of Ag, Cr, Cu, Hg, Ni, Pb, PCBs, DDT, Chlordane, Dieldrin, LMW-PAHs and HMW-PAHs, and that concordance between mussels and sediments exists in both urban and rural sediments. For Zn, Cd, and As there is no correspondence between mussels and sediments. Except for DDT and Zn, contaminant levels in oysters, on the other hand, do not rank in parallel to those in sediments.

In summary, sediments are the preferred matrix with which to describe spatial distributions of contamination. Mussel analyses will mirror the sediment results for most contaminants and oyster analyses will generally not reflect sediment data. Annual-scale temporal trends, on the other hand, are much more readily described through bivalve analyses.

6.3 Sediment Quality Standards and their Underlying Philosophy

6.3.1 Philosophy and approach in the Netherlands

Leendert van Geldermalsen presented the paper prepared by the Dutch Ministry of Housing, Physical Planning and Environment on the underlying philosophy of soil and sediment quality standards in the Netherlands. He emphasized the different roles, goals and functions that groups who deal with environmental issues have. These so-called "blood groups", their aims and functions are given in Annex 8. It must be clear that managers and politicians are using quality standards and normalization for other purposes and from other points of view than scientists do. Managers and politicians are only interested in comparable data to execute a policy and to evaluate whether the goals of those policies are or can be achieved. The paper states the goal of the Dutch environmental policy, which is to bring about a physical and chemical environment that is healthy for people, plants and goods and that can fulfill long-lasting functions for society and nature. This leads to the formulation of the Dutch environmental policy for soils and sediments that the soil must be fit to use for its 'natural' function. This means for instance that soils and sediments must be 'ecologically healthy' in order to be able to serve as a safe dwelling place for living creatures and plants. This goal calls for an environmentally directed approach of standardization. This was achieved by sampling and analyzing a great number of 'ecologically healthy' locations.

Because of the fact that the samples were judged on their environmental quality, digestion with aqua regia was found sufficient. The so-called Reference Values for the heavy metals of such an 'ecologically healthy' soil are defined by this exercise as a function of the fraction <2 µm and of total organic matter. The amount of heavy metal can now be given by a mathematical formula which is given in Annex 9. Since there was too little information on organic micropollutants, here the quality standards were derived from a calculation using drinking water standards, organic matter content, and partition coefficients of these micropollutants from the literature. These are also given in Table 3 of Annex 9.

These quality standards are now used in Dutch environmental policy, for instance in the rules and regulations for the dumping of dredged materials. A U.S. consulting firm used a similar approach to calculate apparent effects thresholds (see Annex 10). It yields, however, different values, probably due to the fact that only data from Puget Sound were taken into account.

6.3.2 Procedures and Criteria for the Selection of Dredged Material from Dutch Harbors for Disposal at Sea

Leendert van Geldermalsen also explained the Dutch rules and regulations for the dumping of dredged material at sea. The dredged material should meet a quality and a quantity condition. Additionally, the impact of dredged material disposal on the quality of the receiving water system must be taken into account. Annex 9 shows how these conditions were worked out. The conditions will become more rigid in the future until all dredged material that must be dumped in the sea has a near 'natural' or 'background' quality.

7 PROGRESS IN INTERCOMPARISON PROGRAM ON ANALYSIS OF CBs AND PLANS FOR SECOND STAGE FOR SEDIMENTS

The Chairman reviewed the history of the current ICES/IOC intercomparison program for analyses of CBs, and the role that WGMS will play in future stages. He noted that the coordinators of the first stage (Jacob de Boer and Jan Duinker) had been delayed in distributing intercomparison samples due to the difficulty of obtaining some of the CB congeners at sufficient purity. However, all problems were resolved and the materials are now being distributed. Approximately 100 laboratories are participating, in association with ICES, Oslo and Paris Commissions, and IOC programs. Results are due to be sent to the coordinators by the end of May, 1989. The Chairman has agreed to assist the coordinators in the evaluation of the returned data, as has a member of the WGSATM. It is possible that the evaluation will indicate that the first stage should be repeated. In this case, the coordinators will prepare new materials and distribute them. Laboratories that still do not perform well on the second try will not be invited to participate in future stages of the intercalibration program. Once a decision to proceed to stage 2 is reached, the WGMS will be responsible for conducting the sediment-based portion of the intercomparison. Tom O'Connor reaffirmed the intent of NOAA to conduct this effort for the WGMS.

Matti Perttilä asked whether any ICES guidelines existed for the planning of intercomparison exercises. He felt that such guidelines might reduce the time it takes to plan such exercises, especially given the current practice of involving WGSATM in exercises conducted by other working groups. Herb Windom agreed that it would be more efficient if generic guidelines could be prepared by WGSATM. The WG agreed to make a recommendation to ICES on this matter.

8 PROGRESS IN THE PREPARATION OF THE CRITICAL ASSESSMENT OF CONTAMINANTS IN BALTIC SEA SEDIMENTS

Matti Perttilä introduced his paper that reviews this topic and describes the present status. To study the possibilities of trend monitoring of contaminants in Baltic Sea sediments, a Sub-Group on Baltic Sediments was set up in 1982 under the ICES Working Group on the Baltic Marine Environment. According to its terms of reference, the sub-group, chaired by Matti Perttilä, should compile a critical review of contaminant and geochemical data from sediment studies carried out in the Baltic Sea, and consider the possibilities of starting a pilot monitoring study. The sub-group coordinated an intercomparison exercise in 1984, the results of which have been reported to ICES by Dr. Brügmann. Apart from purely analytical discrepancies, there still exist differences of opinion as to whether "total" or "biologically available" metal contents in sediment should be used for monitoring purposes, and how the latter should be defined.

A meeting of the subgroup was held in Tallinn, USSR, in September 1988, in order to discuss the contents of the review and to decide on the authors. It was agreed that the review should contain two different types of maps in addition to text. One map should describe the general distribution of soft bottom areas, as these would probably be the most suitable areas for contaminant monitoring studies. The other type of map should show the location of those few stations where contamination studies and age determinations have been carried out reliably for a long time.

The distribution of the following elements and compounds should be illustrated in the maps (where appropriate data exist):

- trace elements - Zn, Cu, Pb, Cd, Hg
- organochlorines - PCB, DDT, DDD, DDE, HCH, HCB
- petroleum hydrocarbons
- phosphorus and nitrogen
- organic carbon

Responsibility for collecting and sending in the data to the chairman of the sub-group for drafting the maps was accepted by several members.

A draft review was scheduled to be presented at the next WGBME meeting in April 1989. The preparation of the draft is, however, still uncertain. This is so mainly because participation in the September meeting turned out to be very poor. However, the subgroup will attempt to reach conclusions regarding initiation of a sediment monitoring program in the Baltic at its next meeting in April, 1989. It is now planned that the critical review will be ready for the 1990 meeting.

9 ANY OTHER BUSINESS

The WG reviewed the paper by Uthe *et al*. on "Sampling Strategies for Trend Monitoring Using Biota, Sediments and Seawater", referred to in Section 2.2.3 of this report. The WG accepted the responsibility of completing the sections of this paper dealing with sediments. There was a feeling that much of the material missing from the paper, especially information regarding guidelines for use of sediments in monitoring, existed in various reports from WGMS. Herb Windom agreed to compile all past reports and advice from WGMS and to prepare annotations on each describing the significant contents of each report. Based on his compilation, the WG will determine how best to provide the input needed to complete the sediment-related portions of the paper started by Uthe *et al*.

Doug Loring introduced a paper that he and R. Rantala had prepared, entitled "Total and partial methods of digestion for estuarine and coastal sediments and suspended particulate matter". He noted that this paper was prepared at the request of ICES to accompany the videotape that he had prepared last year. The WG concluded that, with a few minor changes, it was suitable for publication in the ICES Techniques in Marine Environmental Sciences series. Doug Loring agreed to amend the paper accordingly and submit it directly to ICES for publication.

The WG reviewed a paper by B. Larsen and A. Jensen entitled "Evolution of the sensitivity of sediments in pollution monitoring". The WG took note of the addition made to a previous version of the paper and felt that the paper is an important contribution. The WG commended the authors for their efforts and encouraged their plan to submit the paper to the *Marine Pollution Bulletin*.

Jens Skei introduced two relatively new books of probable interest to WG members and distributed copies of the title pages to assist members in obtaining copies of these books.

The Acting Chairman introduced the subject of finding a permanent chairman for the WG. It was generally agreed that the present circumstances were not fair either to the Acting Chairman or to the WG, because it has been poorly represented in various ICES meetings. Herb Windom stated that he thought the Acting Chairman had done an outstanding job and hoped that he would agree to continue as Chairman. By acclamation, the WG endorsed this statement. John Calder thanked the WG for their expression of confidence and stated that he would be willing to serve as Chairman for at least one additional year.

10 RECOMMENDATIONS AND ACTION LIST

The Acting Chairman reviewed the action items and recommendations agreed to by the WG. After additional clarification, they were accepted in final form and appear as Annex 11 and Annex 12, respectively, to this report.

11 DATE AND VENUE OF NEXT MEETING

The WG agreed that it was not necessary for the next meeting to be held in conjunction with any other ICES group. Because preparation of the report was being handled primarily by the Chairman and rapporteur, the meeting could occur as late as early May of 1990 and the report still could be available for the ACMP meeting in June. The members from both Portugal and the Netherlands expressed interest in hosting the next meeting. The WG expressed the view that they would welcome either invitation. Tereza Vinhas and Leendert van Geldermalsen will pursue the matter further at home and report back to the Acting Chairman in the near future. With this information, the Acting Chairman will consult with ICES to determine the exact date and venue for the next meeting.

12 ADJOURNMENT

After thanking Herb Windom for the splendid facilities and support provided, and thanking the WG members for their lively participation, the Acting Chairman closed the meeting at 17.30 hrs on 22 February 1989.

ANNEX 1

WORKING GROUP ON MARINE SEDIMENTS IN RELATION TO POLLUTION

Savannah, Georgia, USA
20 - 23 February 1989

AGENDA

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ANNEX 2

WORKING GROUP ON MARINE SEDIMENTS IN RELATION TO POLLUTION

Savannah, Georgia, USA
20 - 23 February 1989

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ANNEX 3

WORKING GROUP ON MARINE SEDIMENTS IN RELATION TO POLLUTION

Savannah, Georgia, USA
20 - 23 February 1989

LIST OF ABBREVIATIONS AND ACRONYMS

ACMP = ICES Advisory Committee on Marine Pollution

GEMSI = IOC/UNEP Group of Experts on Methods, Standards, and Intercalibration

GESRM = IOC/IAEA/UNEP Group of Experts on Standards and Reference Materials

ICES = International Council for the Exploration of the Sea

IOC = Intergovernmental Oceanographic Commission

JMG = Joint Monitoring Group of the Oslo and Paris Commissions

JMP = Joint Monitoring Programme of the Oslo and Paris Commissions

MCWG = ICES Marine Chemistry Working Group

SACSA = Standing Advisory Committee for Scientific Advice of the Oslo Commission

TIMES = Techniques in Marine Environmental Sciences

WG = Working Group

WGBEC = ICES Working Group on Biological Effects of Contaminants

WGBME = ICES Working Group on the Baltic Marine Environment

WGEAMS = ICES Working Group on Environmental Assessment and Monitoring Strategies

WGMS = ICES Working Group on Marine Sediments in Relation to Pollution

WGSATM = ICES Working Group on the Statistical Aspects of Trend Monitoring

UNEP = United Nations Environment Programme

ANNEX 4

GUIDELINES FOR DIFFERENTIATING ANTHROPOGENIC FROM NATURAL TRACE METAL CONCENTRATIONS IN MARINE SEDIMENTS
(NORMALIZATION TECHNIQUES)

EXECUTIVE SUMMARY

Marine sediments contain natural concentrations of metals. They may also contain additional anthropogenic contributions. The purpose of this document is to provide advice on the analysis of metals in marine sediments and the evaluation of the resulting data that will enable the natural and anthropogenic contributions to be estimated separately. It is further hoped that the methods described will allow for a better comparison of metal data from different regions, resulting from various national and international programs.

The following major points must be stressed. This document only relates to metals in marine sediments, not other contaminants. Techniques described require total digestion of total sediment samples. Total digestion (HF + aqua regia) is required because it is the only way analyses of sediments from different regions can be compared. It is also the only means by which analyses can be standardized, or intercalibrated, since all standard reference materials are certified for total digestion. The procedures described in this document are not recommended to the exclusion of all others, but as minimum requirements for the purposes stated above. Thus, it is recognized that additional analyses of specific sediment size fractions or partial digests may be desirable to address specific regional questions.

The term "normalization" is used in this document to refer to techniques where metal concentrations are related to physical or chemical parameters of natural sediment from a given area. Based on such relationships, unnatural or anthropogenic metal contributions to contaminated sediments can then be estimated using the metal concentration divided by the "normalization" parameter.

Finally, this document should be used to provide general advice on approaches to normalizing sediment metal data. For specific examples of approaches to normalization, the reader is referred to Loring (1987b), Windom <u>et al</u>. (1989), FLA-DER (1988).

1 <u>Introduction</u>

The purpose of these guidelines is to present a set of normalization techniques that can be used to evaluate the concentrations of metals in sediments with respect to background or natural levels expected for similar non-contaminated deposits. Although these techniques have been proven effective in many areas, their applicability must be demonstrated in new areas of study. Once the techniques have been shown to permit determination of the natural levels of trace metals in the sediments under study, the excess levels above background values could then be used to establish sediment quality criteria.

Most contaminants (metals) show high affinity to particulate matter and are, consequently, enriched in bottom sediments of estuaries and coastal areas adjacent to industrial and urban areas. In practice, natural and anthropogenic substances entering the marine systems are affected by a variety of biogeochemical processes. As a result, they become associated with fine grained suspended solids and colloidal organic and inorganic particles. The ultimate fate of these substances is determined to a large extent by particulate dynamics and they tend thus to accumulate preferentially in areas of low hydrodynamic energy.

It is, therefore, essential to understand, and normalize for, the effect of grain size distributions and geochemical origin on natural metal variability before the magnitude of anthropogenic metallic inputs can be realistically evaluated. For any study of sediments, a basic amount of information on their physical and chemical characteristics is required before an assessment can be made on the presence or absence of anomalous metal concentrations. The concentration at which contamination can be detected depends on the sampling strategy and the number of physical and chemical variables that are determined for individual samples.

The interpretation of the data generally requires that the chemical composition of the sediments from a selected area be compared to background or natural values found in uncontaminated sediments (see, for example, FLA DER, 1988). The determination of the relation between the concentration of contaminants and various characteristic parameters related to the size distribution and to the mineralogical composition of the sediment is required to normalize for the grain size effect and to allow identification of anomalous metal concentrations within estuarine and coastal sediments. The various granulometric and geochemical approaches used for the normalization of trace metal data as well as the identification of contamination in estuarine and coastal sediments has been extensively reviewed by Loring (1988). The first approach is purely physical and consists of characterizing the sediment by measuring its content of fine material. The second approach is of a chemical nature and is based on the fact that the small size fraction is usually rich in clay minerals, iron and manganese oxihydroxides and organic matter. Chemical parameters (e.g., Al, Li, Sc, etc.) representative of these components may thus be used to characterize the small size fraction under natural conditions. Furthermore, these components often exhibit a high affinity for organic and inorganic contaminants and are responsible for their enrichment in the fine fraction.

It is strongly suggested that several parameters be used in the evaluation of sediments because the types of information which may be gained by the utilization of these various parameters are often complementary and extremely useful considering the complexity and diversity of situations encountered in the sedimentary environment. Furthermore, the measurements of the parameters selected here are rather simple and inexpensive.

This report presents general guidelines for sample preparation, analytical procedures, and interpretation of physical and chemical parameters used for the normalization of geochemical data. Its purpose is to demonstrate how to collect sufficient data to normalize for the grain size effect and to allow detection, at various levels, of anomalous metal concentrations within estuarine and coastal sediments.

2 Sampling Strategy

Ideally, a sampling strategy should be based on a knowledge of the source of pollutants, the transport pathways of particulate matter and the rates of accumulation of sediments in the region of interest. However, existing data are often too limited to define the ideal sampling scheme.

The high variability in the physical, chemical and biological properties encountered in sediments implies that an evaluation of sediments in a given area must be based on a sufficient number of samples. This number can be evaluated by an appropriate statistical analysis of the variance within and between samples. To test the representativity of a single sediment specimen at a given locality, several samples at one or two stations should be taken.

The methodology of sampling and analysis should follow the recommendations outlined in "Guidelines for the Use of Sediments as a Monitoring Tool for Contaminants in the Marine Environment" (Section 15 of the 1986 Report of the ICES Advisory Committee on Marine Pollution, Coop. Res. Rep. No. 142 (1987)). In most cases, the uppermost layer of sediments collected with a tightly closing grab sampler (level 1 in the Guidelines) is sufficient to provide the information concerning the contamination of the sediments of a given area compared to sediments of uncontaminated locations or other reference sediments (spatial trend assessment).

Another valuable advantage of using sediments for monitoring is that they have recorded the historical evolution of the composition of the particulate matter deposited in the area of interest. Under favorable conditions, the degree of contamination may be estimated by comparison of surface sediments with deeper samples, taken below the biological mixing zone. The concentrations of trace elements in the deeper sediment may represent the natural background level in the area in question and can be defined as a baseline value. This approach requires sampling with a box-corer or a gravity corer (levels 2 and 3 in the Guidelines).

ANALYTICAL PROCEDURES

Typical analytical procedures to be followed are outlined in Table 1. The number of steps that are followed will depend on the nature and extent of the investigation.

GRAIN SIZE

It is recommended that, at least, the amount of material < 63 µm in size and the total trace metal concentrations be determined for each sample. An isolated size fraction of the total sediment may be used for subsequent analysis if required to determine the absolute metal concentrations in that fraction, providing that its contribution to the total is kept in perspective when interpreting the data. Such size-fraction data might be useful in tracing the regional dispersal of metals associated with a specific size fraction, providing the provenance of the material remains the same.

SAMPLE PREPARATION

Sediment samples for trace metal analyses preferably should be freeze-dried, or air or oven dried. Freeze drying is preferred to air or oven drying because it results in a powdery material instead of hard clay aggregates or crusts; loss of any volatile Hg is also avoided by this method.

Material > 2 mm, such as pebbles, coarse organic fibers, and shells, are removed. The remaining material is crushed and homogenized before being split into sub-samples designed for various chemical analyses. The sub-samples should, in order to avoid contamination, be obtained with plastic utensils. After drying, the various sub-samples are placed in a dessicator and/or stored in air-tight plastic vials until required for future use. Separate samples, stored in glass, are kept for mercury analysis.

The water content should be measured because it allows a salt content correction factor to be calculated in sediments of high water content, and allows one to go from measurements of sedimentation rates (mm per year) to mass accumulation rates when radiochemical analyses are performed.

CHEMICAL ANALYSES

It is recommended that the whole unfractionated sample be analyzed to determine its total metal concentrations. This is because total metal concentrations determine the true extent of metal levels in the sediments. They are the criteria by which the extent, if any, of contamination is evaluated and on which national and international dredging and dumping regulations are based. For example, the Canadian Ocean Dumping Control Act (ODCA) limits the dumping of material containing > 0.6 mg/kg Cd and > 0.75 mg/kg Hg in the total sample. The total content of elements can be determined by non-destructive methods, such as X-ray fluorescence or neutron activation, or by complete digestion of the sediments followed by methods such as atomic absorption spectrophotometry or emission spectroscopy.

A number of sub-samples are required for analyses (Table 1). A 0.1 - 1 gram subsample is required for the determination of the total metal concentrations and should be well homogenized.

Selection of Metals

The selection of trace metals to be determined depends on the purpose of the investigation. Usually Hg and Cd are considered to be the most environmentally critical metals, followed by Pb. In addition, the concentrations of Zn and Cu are usually determined.

For normalization purposes, determinations of at least Al and Li are recommended, followed by Fe and Mn in order to account for the metal variations in respect to the variations of the aluminosilicate mineral fraction. Determinations of the carbonate and organic matter or organic carbon contents are also recommended because carbonate may be an important diluent (carrier under certain conditions) and organic matter is an important concentrator of trace metals, particularly Hg and Cd, in the sediments.

Decomposition of Samples for Total Metal concentrations Except Hg

In order to determine the total metal concentration, e.g., by atomic absorption spectrometry (AAS) or inductively coupled plasma atomic emission spectrometry (ICP/AES), it is necessary to decompose the sediment sample in such a way as to release the metals from minerals and compounds with which they are associated. The use of a reliable and repeatable decomposition technique has a decisive effect on the amount and quality of analytical data and is the basic condition for obtaining precise and accurate data.

Hydrofluoric acid (HF) is the only acid that reacts with silicates to form soluble H_2SiF_6 and release metals bound in the silicate lattices. Since silicates form the majority of the mineralogical compounds in marine sediments from northern latitudes, where anthropogenic inputs are highest, it is the only acid solvent that can be used to ensure the complete release of trace metals associated with the silicate phases of sediments. HF is, therefore, an essential ingredient of any wet-chemical procedure for the determination of total metal concentrations in most sediments.

HF combined with aqua regia, which is a mixture of HNO_3 and HCl used to dissolve sulfides and oxides, is the recommended dissolution mixture for sediments. HNO_3, or even aqua regia, digestions alone are not recommended because they do not always remove the total metals and are more sensitive to variations in procedures. Many laboratories employ a mixture of HF, $HClO_4$, and HNO_3. A recent ICES intercalibration exercise (Loring, 1987a) showed that aqua regia alone removes significantly lesser amounts of metals than the HF plus aqua regia dissolutions. In addition, the relative accuracy of the results determined after HF dissolutions can be assessed because the metal values for certified reference materials are based on determinations of total metals. No such reference values are available for materials digested with aqua regia.

A number of procedures exists for the decomposition of sediment samples using HF plus other acids. The use of a closed fluorocarbon vessel (bomb) provides complete digestion and precise and accurate determination of the metals using AAS or ICP/AES. In a typical procedure, a 0.1 - 1 gram sample is dissolved in a mixture of HF and aqua regia within 1 hour in the closed bomb. After dissolution, boric acid can be added to neutralize any excess HF. The details of this procedure for cadmium determination have recently been described by Rantala and Loring (1987). Alternately, an evaporation step replaces the addition of boric acid to rid the solution of excess HF and silica. Subsequent evaporation steps can also be used to reduce excess quantities of other acids, such as $HClO_4$ if it is used.

Determination of Hg

Mercury is usually determined separately from the other metals. Digestion is a critical step in the determination of total Hg. HF dissolution is not usually necessary for the determination of Hg, as little Hg is held in the aluminosilicate minerals. Essentially all the Hg can be liberated using a combined HNO_3/H_2SO_4 or $HNO_3/HClO_4$ digestion procedure and measured using a cold-vapour AAS method, such as that used by Hatch and Ott (1968) or Agemian and Chau (1976). In the presence of cinnabar, HCl should be added. Very careful measurements for Hg are required and the use of reference materials is essential for obtaining precise and accurate Hg data. The recent ICES intercalibration exercise (Loring, 1987a) showed that Hg was the most difficult metal to analyze with good precision and accuracy.

Determination of Carbonate

Carbonate content provides information about the provenance of the sediments. Although carbonates usually contain insignificant amounts of trace metals and act as a diluent, calcareous ore particles of Zn and Pb are known and, under certain circumstances, carbonates can fix contaminants such as Cd. Carbonates can be measured by loss of weight of the sediment after acid leaching, or better, by measuring the amount of CO_2 evolved during acid leaching.

Determination of Organic Carbon

Terrestrial and marine organic carbon is sometimes an important scavenger of and retainer of contaminants, particularly Cd and Hg in sediments (Loring, 1975; Cato, 1977). It also controls to a large extent the oxidation-reduction environment and contributes to the diagenetic process in the sediments. It can be determined in carbonate-free samples by wet-chemical oxidation methods, for easily oxidizable organic carbon or a combustion method for total carbon (from which the carbonate carbon must be subtracted).

NORMALIZATION OF GEOCHEMICAL DATA

Simple to more complex approaches can be used to normalize geochemical data to account for natural variability and identify anomalous metal concentrations. The approach used depends on the requirements and resources of the investigation. Table 2 summarizes the role of various factors for the normalization of trace metal data.

Background Levels

It is necessary to establish natural background metal levels before the extent of heavy metal contamination, if any, can be estimated. Such background levels are subtracted from the total values to yield an estimate of the contamination.

Background levels can be estimated either by:

1) direct measurements of metal concentrations in texturally equivalent subsurface core samples obtained from a depth below any possible contamination or biological mixing, with due consideration given to possible diagenetic effects (e.g., pore water mobilization of metals); or

2) direct measurements of metal concentrations in recent texturally and mineralogically equivalent sediments from a known pristine region.

3) If direct measurements are not available, average metal concentrations in texturally equivalent sediments reported in the recent literature may be used with caution.

In the case of the ratios of metals to reference elements such as Al, the extent of contamination, if any, can be calculated from the equation:

$$EF = (M{:}Al)_x/(M{:}Al)_{rs}$$

where EF is the enrichment factor and $(M{:}Al)_x$ is the metal to aluminum ratio in the sediment under study and $(M{:}Al)_{rs}$ is the metal to aluminum ratio in the natural or reference sediment. The validity of the background values and enrichment factors will depend on the accuracy of the data on natural or reference sediments.

Metal:Grain Size Normalization

It is necessary to reduce or eliminate grain size effects on chemical data from texturally different samples in order to identify the real trends rather than those superimposed by grain size effects. For linear mathematical normalization to be of value the following requirements should be met:

1) Significant granular variations occur between sediment samples.

2) A strong significant relationship, at least at the 95% level (and the 99% level would be preferred), should exist between the metal content and the relevant normalizing parameter.

3) The regression line which expresses the significant relationship should ideally follow the equation $y = ax$ but in reality the equation $y = ax + b$ is most often found.

4) It should be possible to provide accurate and precise analyses of the metal and relevant parameter to limit errors of measurements of x and y that may mask some of the natural variability of the parameters.

One common procedure used to account for trace metal variability is the mathematical normalization to grain size. Application to trace metal data usually shows that decreasing grain size with increasing metal concentrations occurs consistently, but the strength of the relationship depends on the metal and sedimentary environment because of variations in mineralogical composition related to origin rather than particle size.

To establish the relationship between the metal and grain size, the concentrations of metal are plotted against the percentage of the < 63 µm fraction or a proxy for grain size in each sediment. The basis for this is that, if the concentration of the metal is related to changing sediment particles size, the concentration will change with a constant relation to grain size or its proxy.

In most cases, some sort of linear relationship emerges of the general form $y = ax + b$, the strength of which is measured by the correlation coefficient (r). A linear relationship of the form $y = ax$ is uncommon because the sand size fractions usually contain some trace metals, the amount of which can be estimated from the intercept of the Y axis. If the relationship is significant ($p = < 0.05$ or 0.01), a regression line should be calculated and plotted on a graph along with a 95% or 99% prediction band, so that the natural geochemical population of that metal in relation to grain size changes can be defined. This means that there is a 95% or 99% probability that the points which fall outside the prediction band are from a different or anomalous population. Such samples with anomalous metal:grain size ratios may have been subjected to anthropogenic inputs. Before drawing this conclusion, the absence of plotting errors, analytical errors, or anomalous concentrations of detrital heavy minerals containing the metal, such as chromium-bearing magnetite or chromite, must be verified. Such normalization for grain size, of course, is of little value if the grain size of the sediments containing the trace metals is essentially the same, or if an isolated grain size fraction is analyzed.

Metal:Reference Metal Normalization

Metal:reference metal normalization can be used in addition to, or in lieu of, grain size normalization. The assumption is that the reference metal used, such as Al or Li, serves as a proxy for the major natural metal bearing phases (Table 2). Thus, a plot of trace metal *versus* reference metal can be used in the same way as the trace metal to grain size plots to deduce anomalous trace metal concentrations.

In many cases, separate determinations of the grain size distributions are not made or not deemed necessary and a metal proxy for granular variations, such as Al, Fe, Sc, or Li, is used instead. This approach is valid and Al has been successfully used by Windom *et al*. (1987) and many others for normalization of sediments that have not been derived from the glacial erosional products of igneous rocks. It has been shown, however, that Li (Loring, 1987b) or Sc (Ackermann, 1980) can be used for the normalization of glacial sediments and the identification of anomalous metal concentrations. The extent of contamination, however, must be estimated from the determination and subtraction of background levels, as discussed above.

Normalization to Organic Carbon

Often there is a close relationship of the trace metals (Hg, Cd, Pb, Cu, Ni, Zn, V) to organic carbon in sediments (e.g., Loring, 1975, 1984; Cato, 1977, 1983, 1986; Cato *et al*., 1986). To avoid drawing the wrong conclusions when elevated metal concentrations are due only to a corresponding elevation of the organic matter content of the sediment, the "gradient method" was worked out by Cato in 1977. By the use of this method, organic carbon can be used to normalize for natural trace metal variations in the topmost sediment layer in order to determine background levels as well as to detect anthropogenic inputs in estuarine and coastal sediments. The positive and linear relationship between the trace metals mentioned above follows, in general, the equation $y = ax + b$. The slope "a" of the equation could, according to this method, be used to distinguish the degree or level of contamination in the sediment for certain areas (Cato, *op. cit.*). The method could also be used to show the change of the metal load in an area if the method is used on samples taken over an interval of some years. The slope increases with increasing contamination and *vice versa*. The use of this method requires data from the topmost sediment layer and also a wide range of the organic matter content in the samples studied. Otherwise, the statistical treatment will not be good enough to work out the true equation of the relationship. The background slope can be established from a known pristine area. The method can be used without directly measuring the grain-size variation of the sediment.

Multi-element Normalization

A multi-element/component study in which the major and trace metals, along with grain size and organic carbon content, have been measured, allows the interrelationships between the variables to be established in the form of a correlation matrix. From such a matrix, the most significant ratio between trace metal and relevant parameter(s), be it grain size, Al, Li or organic carbon, can be determined and used for normalization, identification of metal carriers, and detection of anomalous trace metal values. Factor analyses can sort all the variables into groups (factors) that are associations of highly correlated variables, so that specific and/or non-specific textural, mineralogical, and chemical factors controlling the trace metal variability may be inferred from the data set (Loring, 1978; Spencer, 1968).

Conclusions

The use of the granulometric measurements, metal/Al, metal/Li, metal/organic carbon or other metal/reference element ratios are all useful approaches towards complete normalization of granular and mineralogical variations, and identification of anomalous metal concentrations in sediments. Their use requires that a large amount of good analytical data be collected and specific geochemical conditions be met before all the natural metal variability is accounted for, and the anomalous metal levels can be detected. Anomalous metal levels, however, may not always be attributed to contamination, but rather could easily be a reflection of differences in sediment provenance.

Geochemical studies that involve the determination of the major and heavy metals, grain size parameters, organic matter, carbonate, and mineralogical composition in the sediments are more suitable for determining the factors that control the trace metal distribution than the measurement of absolute trace metal concentrations in specific size fractions or the use of metal/reference metal ratios alone. Therefore, they are also more suitable for distinguishing between uncontaminated and contaminated sediments.

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Table 1

A TYPICAL APPROACH FOR DETERMINATIONS OF PHYSICAL AND CHEMICAL PARAMETERS IN MARINE SEDIMENTS

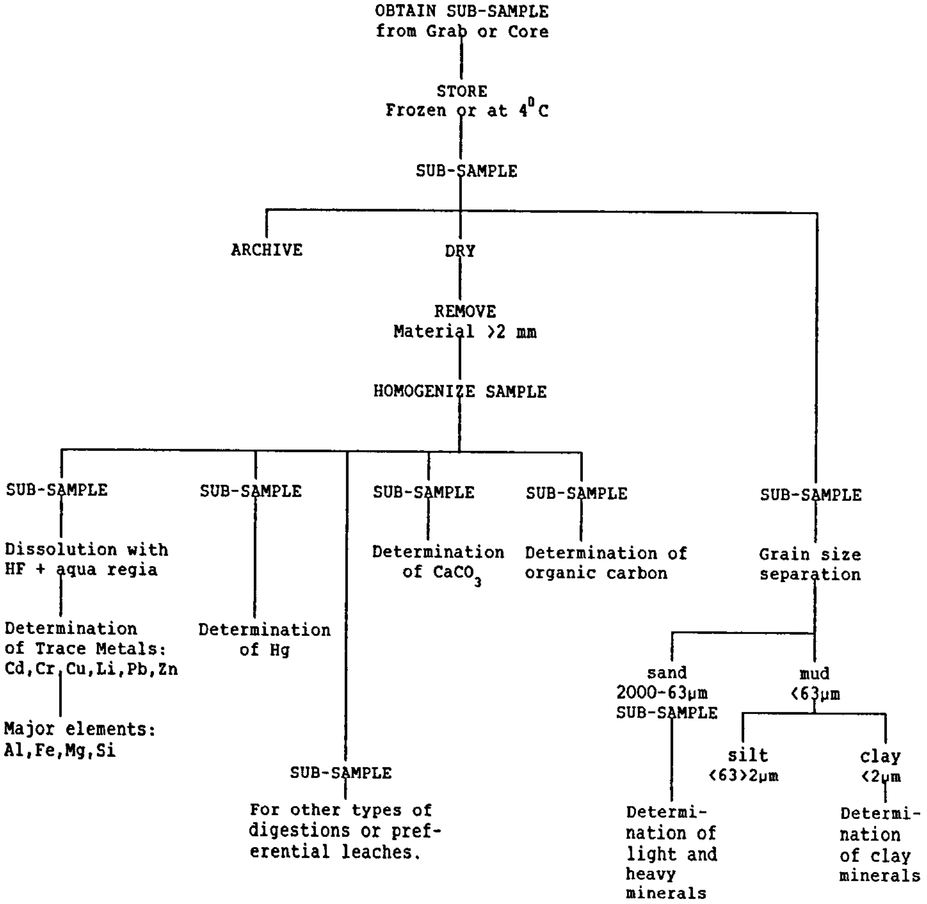

Table 2

SUMMARY OF NORMALIZATION FACTORS

Normalization factor	Size	Indicator	Role
Textural:	µm		Determines physical sorting and depositional pattern of metals
Sand	2000-63	Coarse grained metal-poor minerals/compounds	Usually diluent of trace metal concentrations
Mud	<63	Silt and clay size metal bearing minerals/compounds	Usually overall concentrator of trace metals
Clay	<2	Metal-rich clay minerals	Usually fine grained accumulator of trace metals
Chemical			
Si		Amount and distribution of metal-poor Quartz	Coarse grained diluter of contaminants
Al		Al silicates, but used to account for granular variations of metal-rich fine silt + clay size Al-silicates	Chemical tracer of Al-silicates, particularly the clay minerals
Li, Sc		Structurally combined in clay minerals and micas	Tracer of clay minerals, particularly in sediments containing Al-silicates in all size fractions
Organic carbon		Fine-grained organic matter	Tracer of organic contaminants. Sometimes accumulator of trace metals like Hg and Cd
Fe, Mn		Metal-rich silt + clay size Fe bearing clay minerals, Fe-rich heavy minerals and hydrous Fe and Mn oxides	Chemical tracer for Fe-rich clay fraction. High adsorption capacity of organic and inorganic contaminants
Carbonates		Biogenic marine sediments	Dilutes of contaminants. Sometimes accumulate trace metals like Cd and Cu

ANNEX 5

A GUIDE TO THE INTERPRETATION OF METAL CONCENTRATIONS IN ESTUARINE SEDIMENTS

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EXECUTIVE SUMMARY

This document describes an approach for interpreting metals concentrations in coastal sediments. Interpretation of environmental metals data is made difficult by the fact that absolute metals concentrations in coastal sediments are influenced by a variety of factors, including sediment mineralogy, grain size, organic content, and anthropogenic enrichment. The interpretive tool described herein provides a means of accounting for natural variability of metals and determining whether sediments are enriched with metals with respect to expected natural concentrations.

The interpretive tool is based on the relatively constant natural relationships that exist between metals and aluminum. "Clean" coastal sediments from throughout Florida were collected and their metals content determined. Metal/aluminum regressions and prediction limits were calculated and diagrams of metal/aluminum relationships constructed. Metals data from coastal sediments can be plotted on these diagrams to determine whether measured metal concentrations represent natural concentrations or metal enrichment.

There are several applications of this interpretive tool, including: 1) distinguishing natural versus enriched metals concentrations in coastal sediments, 2) comparing metals concentrations within an estuarine system, 3) comparing metals concentrations in different estuarine systems, 4) tracking the influence of pollution sources, 5) monitoring trends in metals concentrations over time, and 6) determining procedural or laboratory errors.

The guidance in this document is intended for use by regulatory agencies, consultants, and researchers. The geochemical and statistical bases for the interpretive tool, use of the tool, and its limitations are described. Diagrams suitable for reproduction and use as described herein are provided in the Appendix.

PREFACE

The work described in this document is part of broader efforts undertaken by the Florida Coastal Management Program to improve overall capabilities of the state for managing estuarine resources (the "Estuarine Initiative"). This part of the "Estuarine Initiative" suggests improvements in the way environmental data is used in regulatory and resource management decisions. Deficiencies in this area have played a major part in unnecessary regulatory delays, misperception of trends, and other problems in achieving balanced protection and use of coastal resources.

In this respect, the generation and interpretation of metals data have been of priority concern in identifying pollution problems. The purpose of this document is to describe a method for interpreting data on metals concentrations in estuarine sediments based on relationships that exist between metals in natural environments.

Information presented in this document represents refinements of previous work by the Florida Department of Environmental Regulation, Office of Coastal Management (FDER/OCM) and supersedes all previous FDER/OCM guidance concerning metal/aluminum relationships.

If you have any questions or comments about the use of the interpretive tool described in this document, please contact:

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MANAGEMENT ISSUES AND TECHNICAL BACKGROUND

Florida has an extensive coastline (approximately 11,000 miles) and an unusual diversity of estuarine types. Conditions in its many estuaries range from nearly pristine to localized severe degradation. Metals are of particular concern in terms of protecting and rehabilitating estuaries, not only because of their potential toxic effects, but also because high metals concentrations can be a signal for the presence of other types of pollution.

Estuarine management efforts generally suffer from several types of deficiencies in terms of understanding and dealing with metals pollution. Among these are the following:

1. Difficulty in comparing estuarine systems and establishing priorities for management actions.
2. Difficulty in distinguishing actual or potential problems from perceived problems.
3. Unnecessary delays in permitting, attributable to improper generation and interpretation of metals data.
4. Difficulty in establishing cost-effective means for assessing pollution trends and frameworks for understanding overall estuarine pollution.

The problem of understanding metals pollution has at least two major aspects. One aspect involves distinguishing those components attributable to natural causes from those attributable to man's activities. The second aspect involves determining whether metals in anthropogenically enriched sediments are potentially available for recycling to the water column or through food chains in amounts likely to adversely affect water quality and living resources. Guidance in this document deals with the first aspect: the determination of natural versus unnatural concentrations of metals. In doing so, it sets the stage for addressing the second aspect: effects of enriched metal concentrations.

In order to address both of these aspects, it is necessary to have at least a general understanding of the geochemical processes that govern the behavior and fate of metals in estuaries and marine waters. Natural metal concentrations can vary widely among estuaries. In Florida, which has a wide range of estuarine types, this presents special difficulties for making statewide comparisons of estuarine systems and for making consistent, scientifically defensible regulatory decisions. The interpretive approach discussed in this document was developed to account for natural variability in metals concentrations and to help identify anthropogenic inputs.

The tool for interpreting metal concentrations in estuarine sediments is based on demonstrated, naturally occurring relationships between metals and aluminum. Specifically, natural metal/ aluminum relationships were used to develop guidelines for distinguishing natural sediments from contaminated sediments for a number of metals and metalloids commonly released to the environment due to anthropogenic activities. Aluminum was chosen as a reference element to normalize sediment metals concentrations for several reasons: it is the most abundant naturally occurring metal; it is highly refractory; and its concentration is generally not influenced by anthropogenic sources.

To ensure that the information used to develop the interpretive tool was representative of the diverse Florida sediments, uncontaminated sediments from around the state were examined for their metal content and the natural variability of metal/aluminum relationships was statistically assessed.

This approach to the interpretation of metals data was initially described in two documents prepared by FDER/OCM: 1) "Geochemical and Statistical Approach for Assessing Metals Pollution in Estuarine Sediments" (FDER/OCM, 1986a) and 2) "Guide to the Interpretation of Reported Metal Concentrations in Estuarine Sediments" (FDER/OCM, 1986b). Information presented in this document represents further refinements of the approach, using an improved and expanded data base and a more rigorous statistical treatment of metal/aluminum relationships. This document supersedes all previous guidance by FDER/OCM concerning metal/aluminum relationships.

GEOCHEMICAL BASIS FOR AN INTERPRETIVE TOOL USING ALUMINUM AS A REFERENCE ELEMENT

Natural estuarine sediments are predominantly composed of river-transported debris resulting from continental weathering. A schematic representation of the weathering process is given in Figure 1. Acids formed in the atmosphere or from the breakdown of organic matter (e.g., carbonic, humic, fulvic acids) mix with water and form leaching solutions. These leaching solutions break down rocks and carry away the products in solution or as solid debris. The solid debris is composed chiefly of chemically resistant minerals, such as quartz and secondary clay minerals, which are the alteration products of other aluminosilicate minerals. The aluminosilicate clay minerals are represented by the general formula $M \cdot AlSiO4$, where M = naturally occurring metal that can substitute for aluminum in the aluminosilicate structure, Al = aluminum, Si = silicon, and O = oxygen. The metals are tightly bound within the aluminosilicate lattice.

The weathering solution also contains dissolved metals that have been leached from the parent rock. Because of their low solubilities, however, metals are present in the transporting solution (e.g., rivers) in very low amounts, on the order of nanomolar (10^{-9} liter^{-1}) concentrations. Thus, most of the metals transported by rivers are tightly bound in the aluminosilicate solid phases. As a consequence, during weathering, there is very little fractionation between the naturally occurring metals and aluminum.

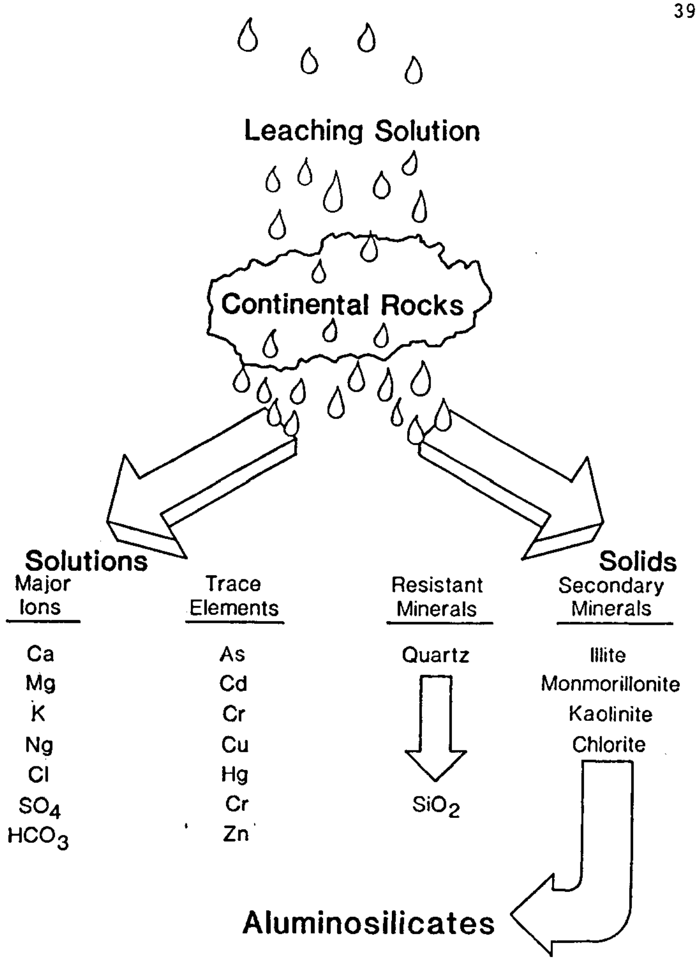


Figure 1. Schematic representation of the weathering process.

In general, when dissolved metals from natural or anthropogenic sources come in contact with saline water they quickly adsorb to particulate matter and are removed from the water column to bottom sediments. Thus, metals from both natural and anthropogenic sources are ultimately concentrated in estuarine sediments, not the water column.

Since much of the natural component of metals in estuarine sediments is chemically bound in the aluminosilicate structure, the metals are generally non-labile. The adsorbed anthropogenic or "pollutant" component is more loosely bound. Metals in the anthropogenic fraction, therefore, may be more available to estuarine biota and may be released to the water column in altered forms when sediments are disturbed (e.g., by dredging or storms).

Aluminum is the second most abundant metal in the earth's crust (silicon being the most abundant). Results from several studies have indicated that the relative proportions of metals and aluminum in crustal material are fairly constant (Martin and Whitfield, 1983; Taylor, 1964; Taylor and McLennan, 1981; Turekian and Wedepohl, 1961). This is not surprising given the lack of large-scale fractionation of metals and aluminum during weathering processes. The average metal concentration of various materials that make up the earth's crust are given in Table 1.

TABLE 1. Relative abundance of metals in crustal materials. Concentration in parts per million (Metal/aluminum ratio x 10-4).

	Average[1] Crust	Upper[2] Crust	Crustal[3] Rocks	Soils[3]	Deep-Sea[3] Sediments	Carbonate[4] Rocks
Aluminum	82,300	84,700	69,300	71,000	95,000	4,200
Arsenic	1.8 (.22)	-	7.9 (1.1)	6.0 (.85)	13.0 (1.4)	1.0 (2.4)
Cadmium	0.2 (.024)	-	0.2 (.029)	0.35 (.049)	0.23 (.024)	0.035 (.083)
Chromium	100 (12)	35 (4.1)	71 (10)	70 (9.8)	100 (11)	11 (26)
Copper	55 (6.7)	25 (3.0)	32 (4.6)	34 (4.8)	200 (21)	4 (9.5)
Iron	56,300 (6800)	35,000 (4100)	35,900 (5200)	40,000 (5600)	60,000 (6300)	3,800 (9000)
Lead	12.5 (1.5)	15 (1.8)	16 (2.3)	35 (4.9)	200 (21)	9 (21)
Manganese	950 (120)	600 (71)	720 (100)	1,000 (140)	6,000 (630)	1,100 (2600)
Mercury	0.08 (.0097)	-	-	-	-	0.04 (.095)
Nickel	75 (9.1)	20 (2.4)	49 (7.1)	50 (7.0)	200 (21)	20 (48)
Silver	0.07 (.0085)	-	0.07 (.010)	0.05 (.0070)	0.1 (.011)	0.1 (.24)
Zinc	70 (8.5)	52 (6.1)	127 (18)	90 (13)	120 (13)	20 (48)

[1] Taylor, 1964.
[2] Taylor and McLennan, 1981.
[3] Martin and Whitfield, 1983.
[4] Turekian and Wedepohl, 1961.

The relative constancy of composition of natural crustal material has been used as the basis of data interpretation by a number of geochemical investigators. Because of its high natural abundance and the relatively small inputs from anthropogenic sources, aluminum has been used to normalize metal data as an aid to interpretation. For example, Duce et al. (1976) compared metal/aluminum ratios in atmospheric dust samples to that of average crustal material to estimate the relative atmospheric enrichment of metals due to anthropogenic sources. Goldberg et al. (1979) used metal/aluminum ratios to evaluate pollution history recorded in sediments from the Savannah River estuary. Trefry et al. (1985) compared lead levels to those of aluminum in sediments of the Mississippi delta to assess the changes in relative amounts of lead pollution carried by the river over the past half century.

If a metal such as aluminum is to be useful to normalize metal concentrations for the purpose of distinguishing natural versus unnatural metal levels in sediments, it must explain most of the natural variance in the concentrations of the other metals. This assumption has been tested for natural sediments along the coast of Georgia (Figure 2, stations along transects HH - GA4). The results of the analysis of over three hundred sediment samples are presented in Figure 3. Metal concentrations are plotted against aluminum; regression lines and confidence limits are also plotted. These results indicate that for this geographic area aluminum does account for most of the variability of the other metals except cadmium. For cadmium, the low natural concentrations are such that analytical uncertainty introduces another source of variance.

The above shows that using aluminum to normalize natural metal concentrations is an approach that works, at least for a relatively localized area. But will this approach work for more diverse sediments such as those of coastal Florida?

Estuarine and coastal sediments of Florida contain natural metal-bearing phases. In south Florida, however, many sediments are carbonate-rich. Inspection of Table 1, indicates that

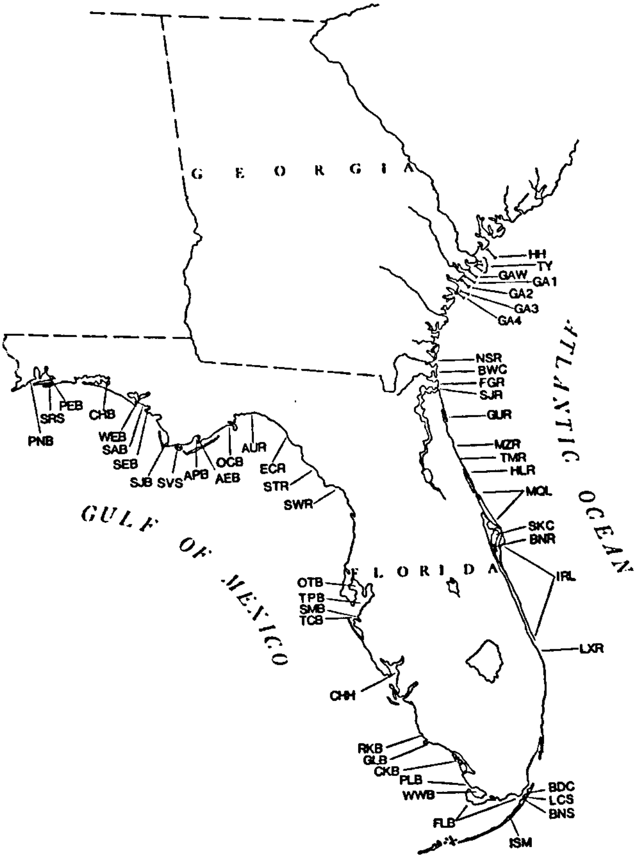


Figure 2. Locations of "clean" natural sediment sample collection sites.

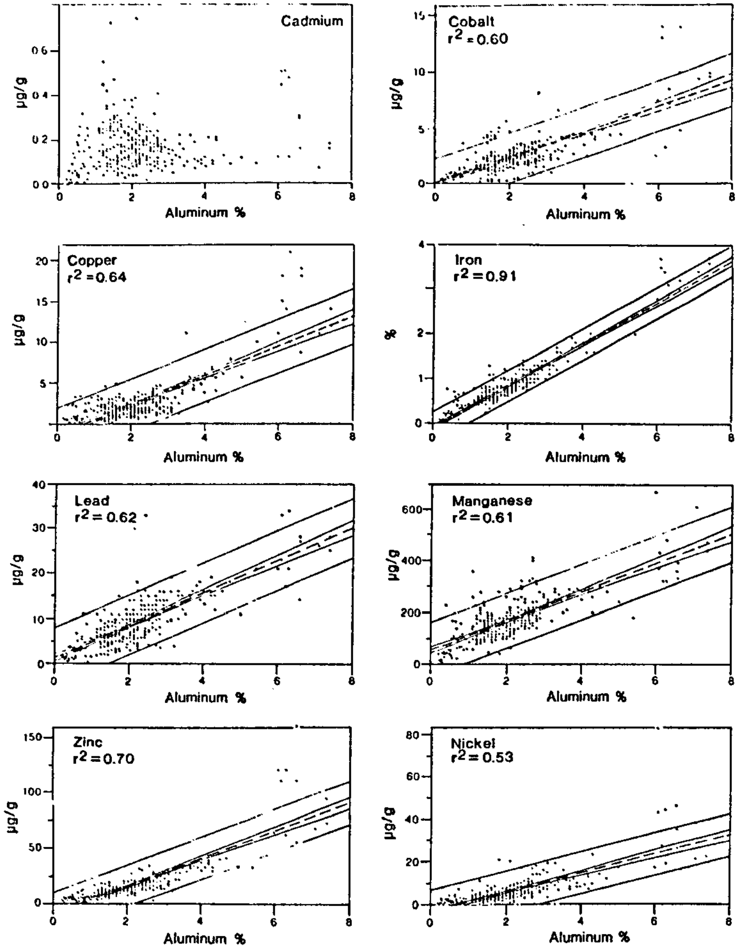


Figure 3. Metal aluminum relationships in sediments off the Georgia coast. Dashed line represents the linear regression line. Solid lines crossing the regression line represent the range in slope at the 95% confidence level. Outer solid lines define the 95% confidence band.

carbonate sediments have larger metal/aluminum ratios than other crustal rocks. Table 1 also suggests, however, that carbonates contain relatively smaller concentrations of most metals as compared to typical crustal material. It follows, therefore, that in a sediment containing a mix of aluminosilicates and carbonates, aluminosilicate minerals would still be the most important metal-bearing phase and that aluminum could still be used to normalize metal concentrations. Thus, aluminum concentrations should also be appropriate for normalizing metal levels in most estuarine and coastal sediments of Florida.

To test whether aluminum can be used to normalize metal concentrations in Florida coastal sediments, sediment samples from 103 stations in uncontaminated estuarine/coastal areas were collected and analyzed for aluminum and a number of environmentally and geochemically important metals. The areas involved encompassed a variety of sediment types ranging from terrigenous, aluminosilicate-rich sediments in northern Florida to biogenic, carbonate-rich sediments in southern Florida (Figure 2). These "clean" sites were selected subjectively, based upon their remoteness from known or suspected anthropogenic metal sources.

At each station, to ensure retrieval of undisturbed sediment samples, divers collected sediments in cellulose-acetate-butyrate cores. Sediment for metals analyses was taken from the upper five centimeters of each core. Duplicate samples were taken at each station and analyzed for nine metals (aluminum, arsenic, cadmium, chromium, copper, mercury, nickel, lead, zinc) according to procedures specified by the United States Environmental Protection Agency (USEPA, 1982), with modifications to enhance accuracy and precision of data from saline environments (FDER/OCM, 1984).

The results of the metals analyses are plotted against aluminum in Figure 4. Superimposed on the graphs are the 95% confidence bands from the Georgia data. These results indicate that aluminosilicate minerals have a major influence on metal concentrations in natural sediments of Florida. It thus appears that sediment metal/aluminum relationships do indeed provide a basis for interpreting metals data from Florida coastal sediments.

DEVELOPMENT OF AN INTERPRETIVE TOOL USING METAL/ALUMINUM RELATIONSHIPS

This section outlines the statistical procedures used to develop a tool for assessing metals enrichment in Florida estuarine sediments, using the data from "clean" estuarine sediments and employing aluminum as a reference element. Two computer programs were used for statistical calculations: MINITAB (Ryan et al., 1982) and SYSTAT (Wilkinson, 1986).

Parametric statistical analyses require that the data under scrutiny have constant variance and be normally distributed. To examine the assumption of constant variance (homoscedasticity), plots of means versus standard deviations were generated for each

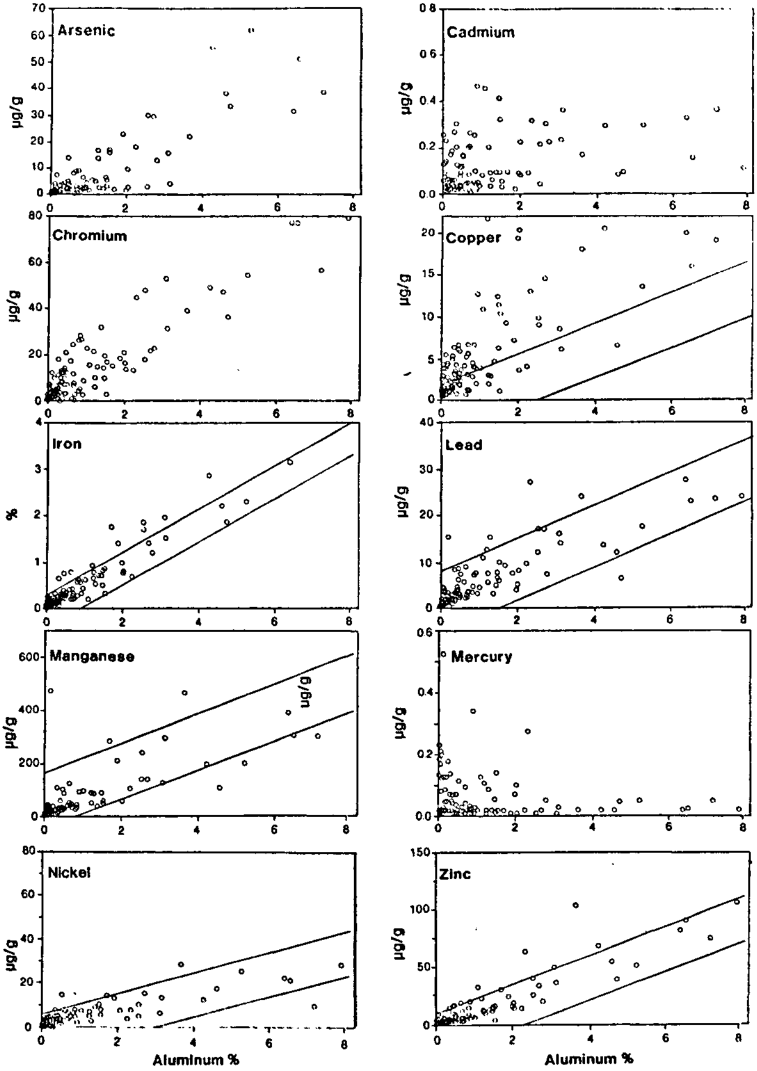


Figure 4. Metal/aluminum relationships in "clean" sediments from Florida estuaries.

metal. Standard deviations were proportional to mean values for all nine metals. After a $\log_{10}$ transformation, the proportionality between standard deviations and mean values was removed, indicating that the assumption of homoscedasticity was satisfied. Examples of these plots before and after transformation, using the data for chromium, are shown in Figure 5.

To examine the assumption of normality, normal score plots were created by calculating normal scores and plotting them against original data. Normal-score plots for untransformed and $\log_{10}$-transformed chromium are shown in Figure 6. The curvature in the plot for absolute chromium concentrations (Figure 6a) indicates that the data are not normally distributed, whereas the relatively linear plot for $\log_{10}$-transformed chromium (Figure 6b) indicates a normal distribution (Wilkinson, 1986). With the exception of nickel, $\log_{10}$ transformation of the remaining metals also appeared to produce normal distributions. The normal distributions of transformed data were confirmed using the probability plot correlation coefficient test (Filliben, 1975). With this test, the null hypothesis (H_O) of normality is examined relative to the alternative hypothesis (H_A) of non-normality. A significantly high correlation coefficient between normal scores and original data results in a failure to reject H_O (i.e., the data are normally distributed). Results of the test are shown in Table 2. Untransformed aluminum, arsenic, cadmium, chromium, copper, mercury, lead, and zinc deviated from normality, whereas

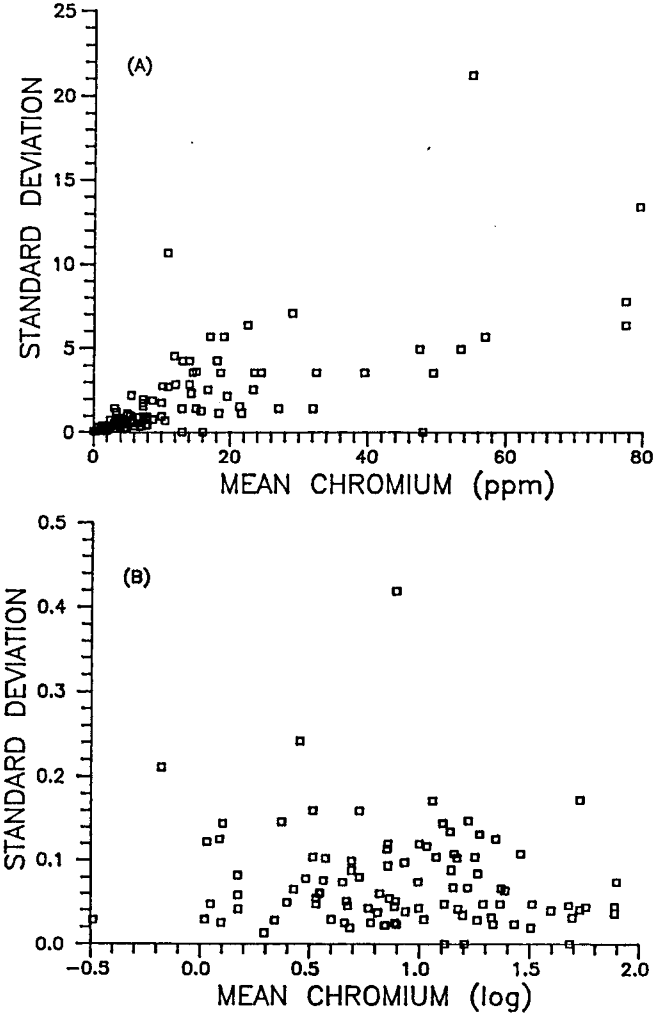


Figure 5. Mean value vs. standard deviation for chromium: A) untransformed data, B) log–transformed data.

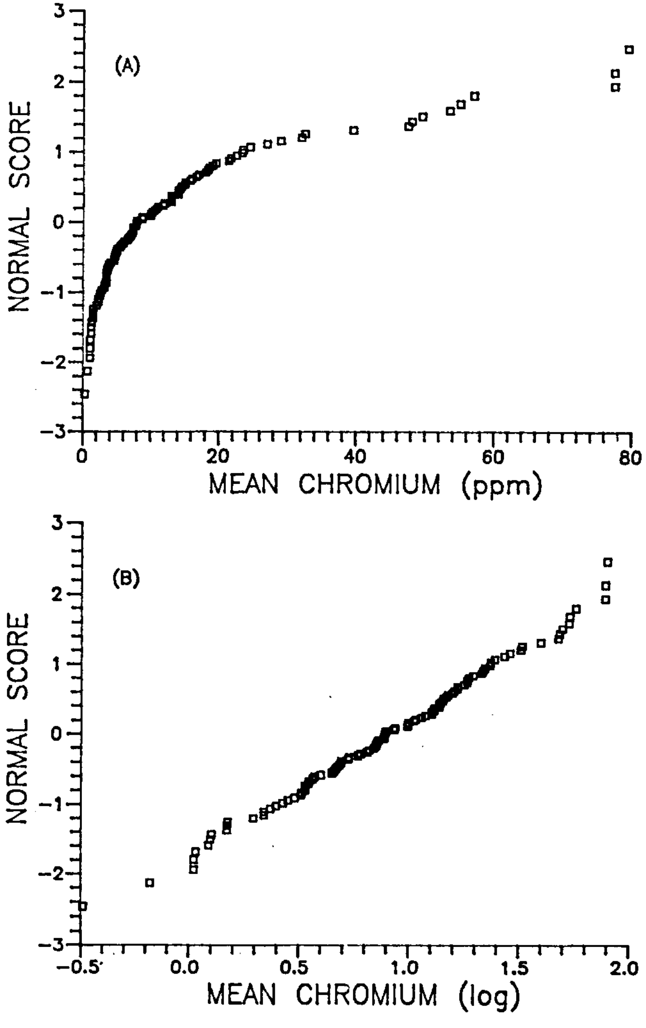


Figure 6. Normal score vs. chromium value:
A) untransformed data, B) log—transformed data.

TABLE 2. Results of probability plot correlation coefficient tests for normality of metals data.

Metal	N	Correlation Coefficient Untransformed	Correlation Coefficient Log_{10}-transformed
Aluminum	103	0.817[c]	0.991[a]
Arsenic	98	0.752[c]	0.988[a]
Cadmium	103	0.920[c]	0.990[a]
Chromium	102	0.847[c]	0.996[a]
Copper	101	0.870[c]	0.992[a]
Mercury	92	0.898[c]	0.981[b]
Nickel	78	0.880[c]	0.986[a,d]
Lead	103	0.885[c]	0.991[a]
Zinc	103	0.778[c]	0.984[b]

[a] $p > 0.05$ (Accept H_0; normal distribution)
[b] $0.05 > p > 0.01$ (Accept H_0; normal distribution)
[c] $p < 0.01$ (Reject H_0; non-normal distribution)
[d] N = 75, Three points (Ni < 0.2 ppm) were removed from data set.

the $\log_{10}$-transformed metals did fit a normal distribution. Log_{10}-transformed nickel data were not normally distributed, being skewed toward low nickel concentrations. The three lowest nickel values (Ni < 0.2 ppm) were removed from the data set, normal scores recalculated, and the remaining nickel data did conform to a normal distribution. For all nine metals, the remainder of the work was performed on $\log_{10}$-transformed data. Metal/aluminum relationships for arsenic, cadmium, chromium copper, mercury, nickel, lead, and zinc are shown in Figure 7. Concentrations of seven metals, arsenic, cadmium, chromium,

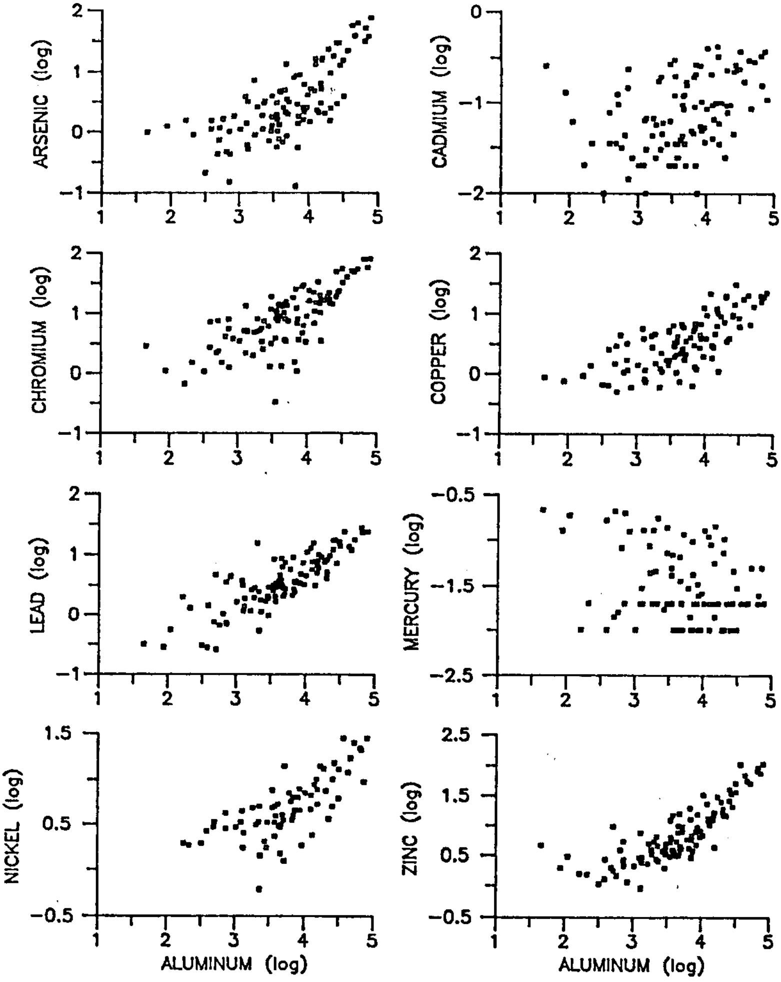


Figure 7. Metal/aluminum relationships for log-transformed metals in clean Florida estuarine sediments.

copper, nickel, lead, and zinc, were positively correlated with aluminum ($p < 0.005$). The strength of the relationships varied among metals as indicated by the magnitude of the correlation coefficient, with cadmium having the weakest relationship (Table 3). Mercury exhibited a weak inverse relationship with aluminum and therefore was excluded from further analysis. The problem of dealing with mercury is discussed in a later section.

TABLE 3. Correlation coefficients for metals and aluminum.

Metal	r	N
Arsenic	0.71[a]	98
Cadmium	0.39[a]	103
Chromium	0.74[a]	102
Copper	0.73[a]	101
Mercury	-0.29[a]	92
Nickel	0.78[a]	75
Lead	0.84[a]	103
Zinc	0.82[a]	103

[a] $p < .005$

Since the selection of stations with "clean" sediment was subjective, it is possible that any given sample was somewhat enriched with one or a combination of metals. In order to minimize the possibility that metal-enriched samples were included in the final data set, metal/aluminum ratios were calculated for arsenic, cadmium, chromium, copper, nickel, lead, and zinc and the probability plot correlation coefficient test was used to determine whether the ratios were normally distributed. If the correlation coefficient test indicated deviations from normality, data points with the largest metal/aluminum ratio were removed (assuming that high ratios were possibly indicative of anthropogenic enrichment) and the process repeated until the metal/aluminum ratios fit a normal distribution. Results are shown in Table 4. Data points for three metals (cadmium, zinc, lead) were deleted from the data set using this procedure.

TABLE 4. Results of probability plot correlation coefficient tests for normality of metal/aluminum ratios.

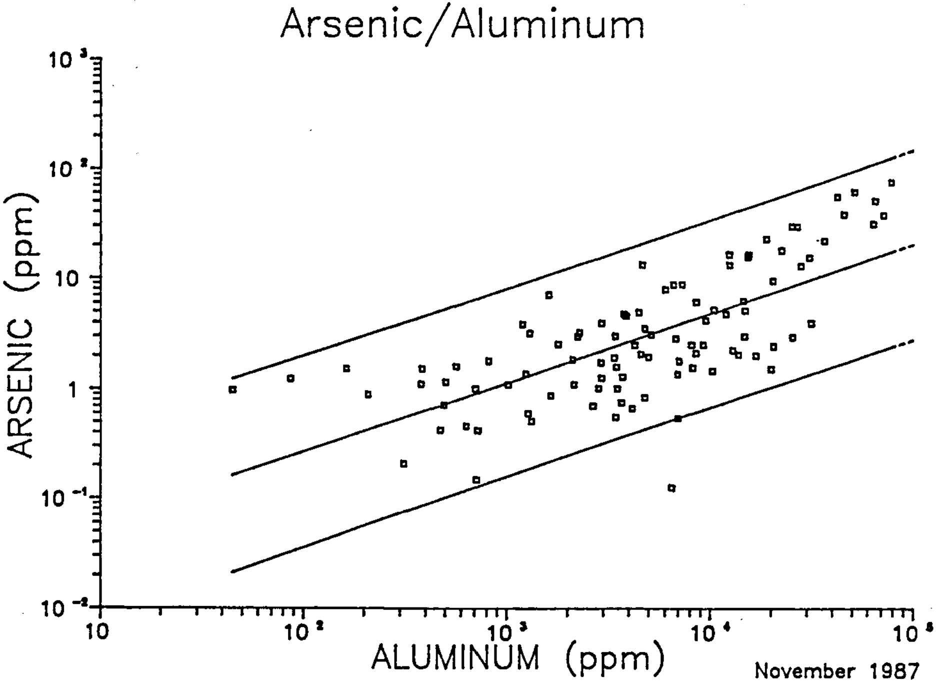
	"Clean" data		"Trimmed-clean" data	
Ratio	N	r	N	r
Arsenic/aluminum	98	0.988[a]	98	0.988[a]
Cadmium/aluminum	103	0.969[c]	102	0.983[b]
Chromium/aluminum	102	0.988[a]	102	0.988[a]
Copper/aluminum	101	0.988[a]	101	0.988[a]
Nickel/aluminum	75	0.911[c]	72	0.987[a]
Lead/aluminum	103	0.955[c]	93	0.993[a]
Zinc/aluminum	103	0.934[c]	99	0.985[b]

[a] $p > 0.05$ (Accept H_0; normal distribution).
[b] $0.05 > p > 0.01$ (Accept H_0; normal distribution).
[c] $p < 0.01$ (Reject H_0; normal distribution).

Nickel again presented a different case, with the distribution of nickel/aluminum ratios being skewed toward low ratios. After removal of three points with the lowest nickel/aluminum ratios, the remaining nickel/aluminum ratios fit a normal distribution. The metals data set resulting from the deletion of points was called the "trimmed clean" data set and was used for subsequent analyses.

Having ascertained that the data does meet the assumptions of normality and homoscedasticity, and having examined metal/aluminum ratios for outlying data points, the data were then analyzed using parametric statistical procedures. Least squares regression analysis, using aluminum as the independent variable and other metals as dependent variables, was used to fit regression lines to the metals of the "trimmed clean" data set (Sokal and Rohlf, 1969). Results of the regressions are presented in Table 5. Correlation coefficients for three of the "trimmed" metals (cadmium, lead, zinc) were greater than those for the original data, indicating the relationship between these metals and aluminum in the "trimmed clean" data set was strengthened by removing the suspect points. Y-intercepts of the regression lines are less than zero because the data were $\log_{10}$-transformed.

Using the regression results, 95% prediction limits were calculated according to Sokal and Rohlf (1969). Regression lines and prediction limits for each metal are plotted in Figures 8-14, superimposed over data points from the "trimmed clean" data set. The relative width of the prediction limits vary among the different metals, depending on the magnitude of the correlation between the metal and aluminum. Metals with the largest correlation coefficients (i.e., lead & zinc) have the narrowest prediction limits.



Arsenic/Aluminum

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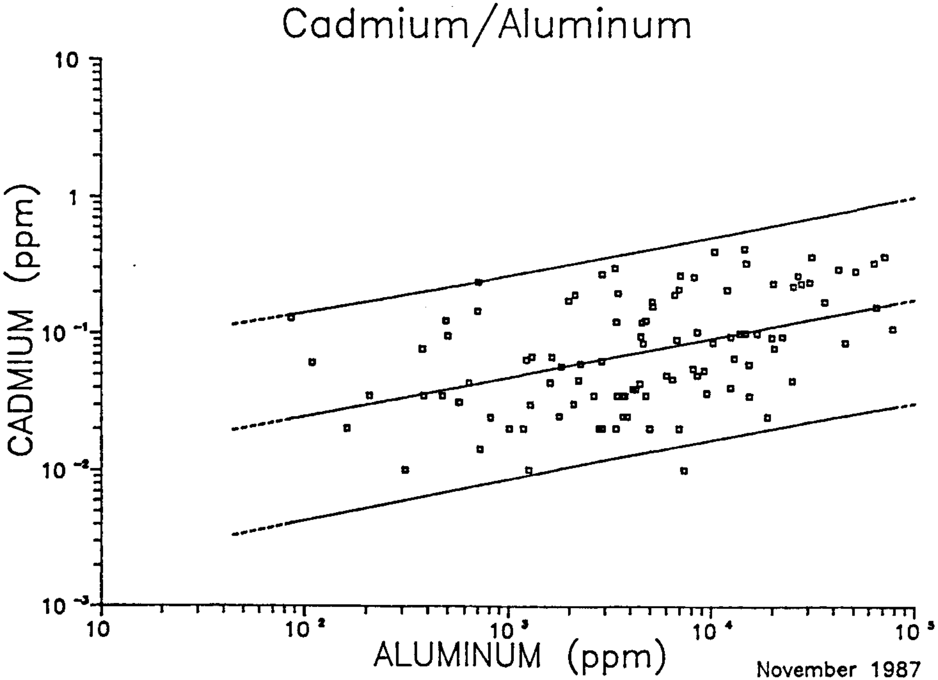
Figure 8. Arsenic/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

Figure 9. Cadmium/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).



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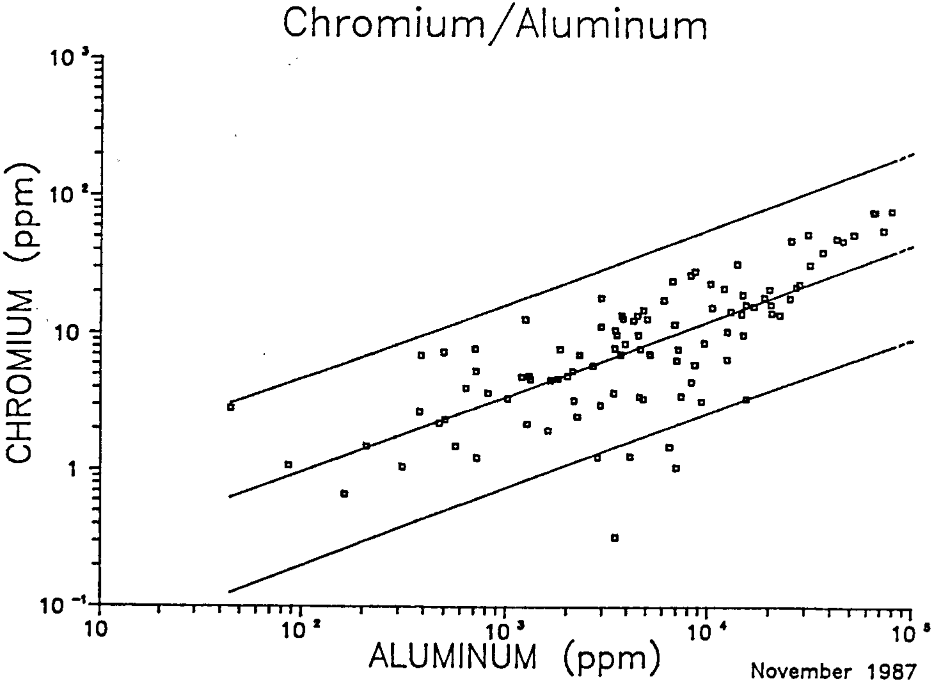

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Figure 10. Chromium/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

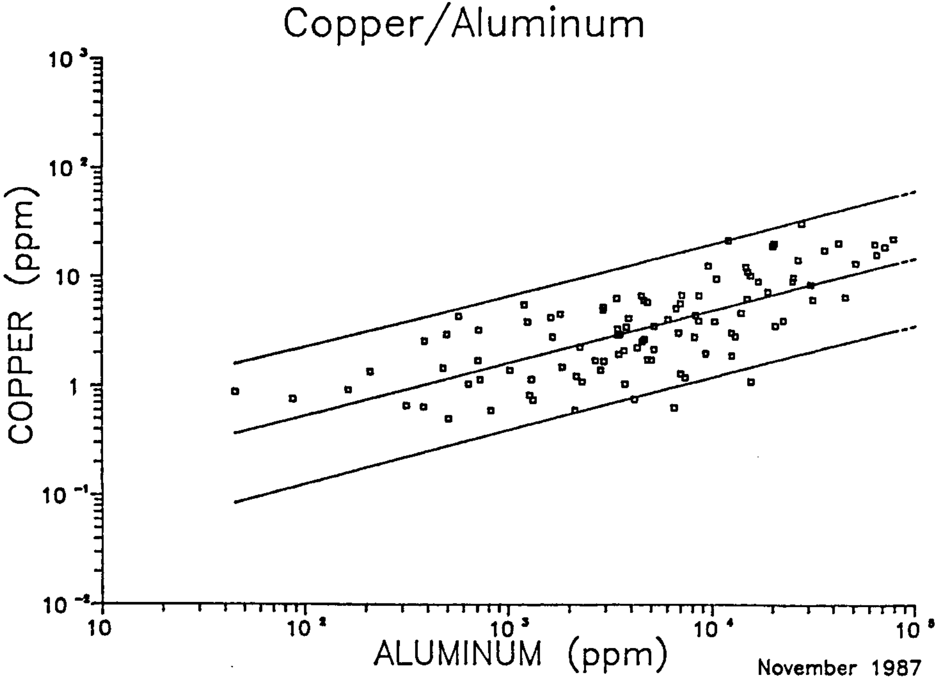

Figure 11. Copper/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

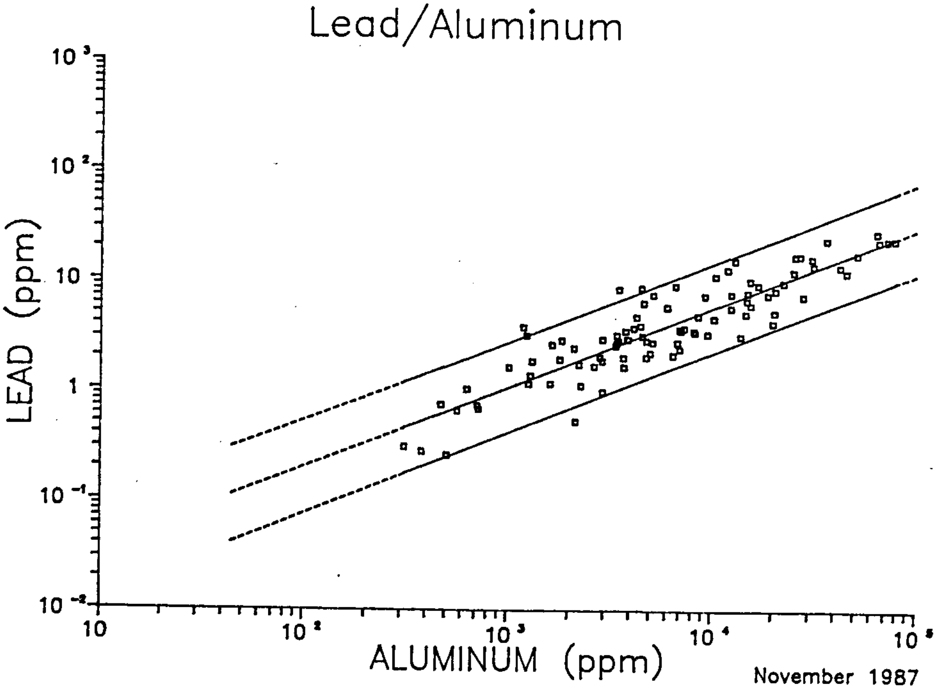

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Figure 12. Lead/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

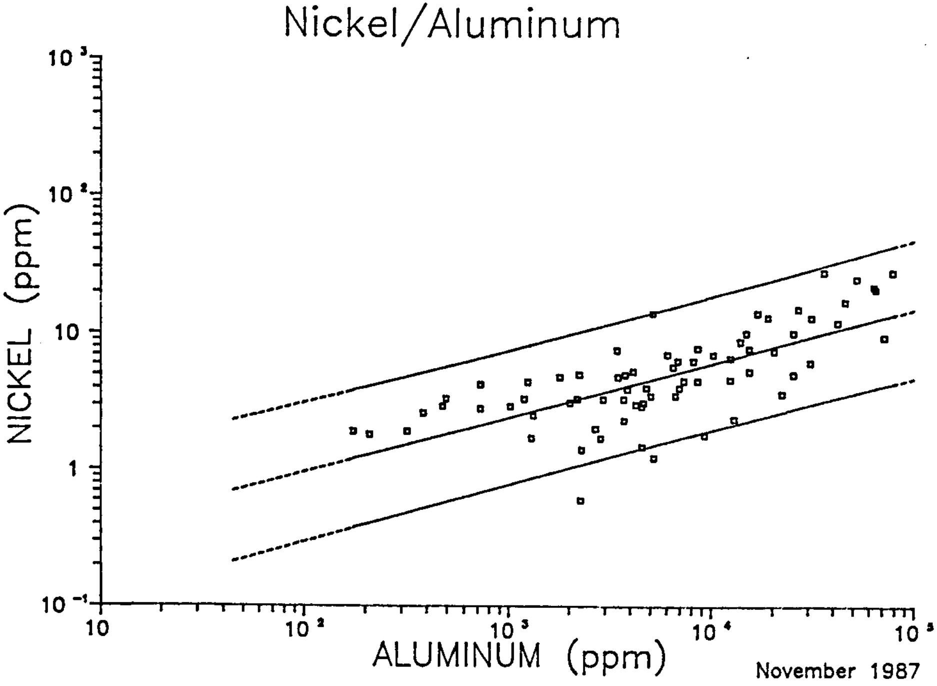

Figure 13. Nickel/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

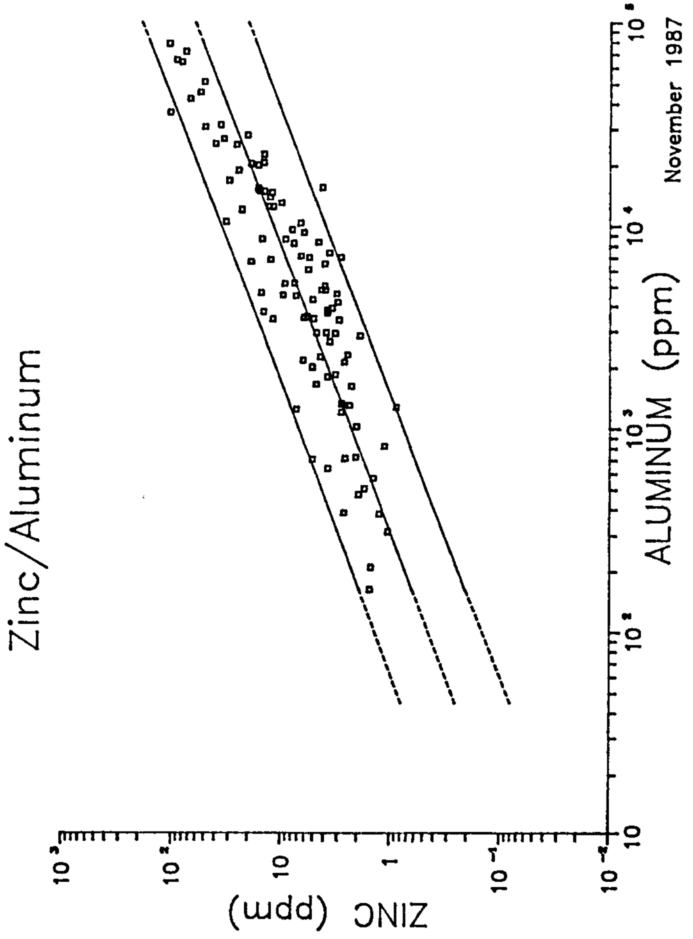

Figure 14. Zinc/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

TABLE 5. Results of regression analyses using aluminum as the independent variable and other metals as dependent variables.

Metal	n	r[a]	a[b]	b[c]
Arsenic	98	0.71	-1.8	0.63
Cadmium	102	0.45	-2.2	0.29
Chromium	102	0.74	-1.1	0.55
Copper	101	0.73	-1.2	0.48
Nickel	72	0.72	-0.81	0.40
Lead	93	0.90	-2.1	0.73
Zinc	99	0.88	-1.8	0.71

[a] Correlation coefficient.
[b] Y-intercept of regression line.
[c] Slope of regression line.

Thus far, it has been demonstrated that statistically significant relationships exist between aluminum and six of the metals examined in "clean" sediments. The calculated regression lines define metal/aluminum relationships and the prediction limits provide a valid statistical estimate of the range of values to be expected from samples taken from clean sediments in Florida. The regression lines and prediction limits presented here can be used to identify unnatural concentrations of metals in Florida estuarine sediments. A similar approach, using iron as the reference element, was taken by Trefry and Presley (1976) to evaluate metals concentrations in northwestern Gulf of Mexico sediments.

USING THE INTERPRETIVE TOOL

Model figures with regression lines and prediction limits are presented in the Appendix. The figures are constructed on a log-log scale to facilitate plotting; absolute metal concentrations can be plotted on the figures without the necessity of $\log_{10}$-transformation. These figures can be reproduced and routinely used to determine whether samples from Florida estuarine sediments are enriched with metals. To do this, a mean value of each metal (derived from replicate or triplicate values) at a station is calculated and points representing corresponding metal and aluminum values are plotted on the appropriate figures. The sediment is judged to be natural or "metal-enriched" depending on where the points lie relative to the regression lines and prediction limits. If a point falls within the prediction limits, then the sediment metal concentration is within the expected natural range. If a point falls above the upper prediction limit, then the sediment is considered to be metal- enriched. Prior to making a determination of "enrichment", however, the accuracy of the analytical results should be confirmed, since an unusual point can also be indicative of procedural errors. Furthermore, since the results are being evaluated with respect to a 95% prediction limit, some points from "clean" stations will lie outside the prediction limit. The farther from the prediction limit, the greater the likelihood that the sample does indeed come from a metal-enriched sediment. Also, greater distance above the prediction limit indicates a greater degree of enrichment.

Points that lie closely above the upper prediction limit must be interpreted in light of available ancillary information about possible sources of metal contamination and information from other nearby stations. Likewise, some points from "clean" sediments will fall below the lower prediction limit. Points that are far below the lower prediction limit should be considered suspect and examined for analytical errors.

APPLICATIONS OF THE INTERPRETIVE TOOL

The interpretive tool using metal and aluminum relationships allows results of sediment chemical analyses to be used for a variety of environmental information needs, including:

1. Distinguishing natural versus enriched metals concentrations in coastal sediments. The degree of enrichment can also be estimated based on the deviation from the expected natural range.
2. Comparing metal concentrations within an estuary. Absolute metal concentrations in coastal sediments will vary depending on many factors, including sediment grain size, mineralogy, and anthropogenic metal sources. Normalizing metals to the reference element, aluminum, allows comparisons of metal concentrations among sites within an estuary.
3. Comparing investigative results from different estuaries. By normalizing metal concentrations to aluminum, an assessment of relative metal enrichment levels can be made, allowing estuaries to be ranked according to specific metal enrichment problems.

4. Tracking the influence of a pollution source. As illustrated in the next section, it is possible to determine the extent of metal-enriched sediments. Delineation of the extent of metal-enrichment can help focus attention on real, rather than perceived, problems.
5. Monitoring trends in metal concentrations over time. By periodically examining sediments at permanent sampling stations or along known pollution gradients, the technique may provide a much-needed device for cost-effective monitoring of the overall "pollution climate" of estuaries.
6. Determining procedural or laboratory errors. The location of points on the metal/aluminum figures can signal possible errors, which could include sample contamination in the field or laboratory, as well as analytical or reporting errors.
7. Screening tool to promote cost-effective use of elutriate or other tests. A variety of tests (eg., elutriate, bioassay) are used to demonstrate potential release to the water column or toxicity of metals in sediments. The interpretive tool described here can be used to reduce the time and cost of testing by screening sediments and selecting for further testing only those whose metal concentrations exceed expected natural ranges. Testing can be limited to the specific metals determined to be enriched during the screening process.

LIMITATIONS OF THE INTERPRETIVE TOOL

The approach presented in this document provides an interpretive tool for evaluating metals concentrations in estuarine sediments. Use of the tool requires knowledge of local conditions and the application of professional judgement and common sense. The following points should be kept in mind when using this interpretive tool.

1) The interpretive tool is useless without reliable data. Results from single, non-replicated samples should never be used. Ideally, sediment samples should be collected in triplicate. If budget constraints dictate analysis of only duplicate samples, the third sample should be archived. In the event of a disparity in the results of replicate analyses, the archived sample should be retrieved and analyzed to resolve the problem.

2) Sediment metals must be carefully analyzed using techniques appropriate for saline conditions and capable of providing adequate detection limits. Because naturally-occurring aluminum and other metals are tightly bound within the crystalline structure of the sediment minerals, the methods for metals analyses must include complete sediment digestion. If aluminum is not completely released by a thorough digestion, metal to aluminum ratios may appear to be unusually high.

3) Mercury presents special problems, both in the laboratory and in the interpretation of results. Since mercury is more volatile than the other metals, a different digestion procedure, employing a lower temperature than for the other metals, must be used. Also, natural mercury concentrations are very near routine

analytical detection limits, where precision and accuracy are reduced. Furthermore, mercury's apparent weak inverse relationship with aluminum precludes the use of aluminum as a reference element.

To deal with mercury, assume that the maximum mercury value in the "clean" sediment data set (0.21 ppm mercury) represents the maximum mercury concentration to be found in natural sediments of Florida. For the purpose of evaluating sediment samples, those containing less than 0.21 ppm mercury can be considered as typical of clean sediments. Samples with greater than 0.21 ppm mercury should be suspected as being enriched and should be interpreted similarly to those other metals that fall outside of the 95% prediction limits.

4) Similar to mercury, natural concentrations of cadmium are also low and are near normal analytical detection limits. Because of this, analytical precision and accuracy are reduced and special care must be taken to obtain accurate laboratory results.

5) Aluminum concentrations in the data set from which these guidelines were prepared ranged from 47 to 79,000 ppm. The data set is, to the extent possible in this project, representative of various types of natural "clean" sediments found in Florida estuaries. The majority of samples recovered from Florida estuarine sediments will have aluminum concentrations within this range.

Some clay-rich sediments, however, especially in northwest Florida, may contain aluminum concentrations exceeding 79,000 ppm. Kaolinite, illite (muscovite), montmorillonite, and chlorite, four commonly occurring marine clays, contain aluminum concentrations of approximately 21%, 20%, 15%, and 10%, respectively (calculated based on chemical formulas for the clay minerals given in Riley and Chester, 1971). Theoretically, therefore, the maximum aluminum concentration in a natural marine sediment is about 210,000 ppm (21%), if the sediment is composed of pure kaolinite. Since sediments are not pure clay, the aluminum concentration in estuarine sediment samples should be considerably less than this theoretical maximum and only in a few instances should aluminum concentrations exceed 100,000 ppm (10% aluminum). Any samples containing greater than 100,000 ppm aluminum should be examined carefully for evidence of contamination or analytical error.

In order to extend the applicability of the interpretive tool to sediments containing aluminum in excess of 79,000 ppm, the regression lines and prediction limits have been extrapolated out to an aluminum concentration of 100,000 ppm. (Since the calculations were done on $\log_{10}$-transformed data, the extrapolation was from 4.9 to 5.0 log units. Aluminum values in the data set ranged from 1.7 to 4.9 log units.) The extrapolations are indicated on the figures by dashed lines. This is considered to be a reasonable approach. However, any interpretations based on the extrapolated lines should be qualified with a statement acknowledging that the data in question exceeds the range of the "clean" data set from which these guidelines were prepared.

6) During the construction of the "trimmed clean" data set, some points containing low aluminum values were removed from the

cadmium, lead, nickel, and zinc data. Since, however, the lowest overall aluminum value was 47 ppm, the regression lines and prediction limits for these four metals have been extrapolated down to an aluminum value of 47 ppm. These extrapolations are also indicated by dashed lines.

7) At stations where a metal's concentration exceeds the 95% prediction limit, the metal must be considered "enriched". One must not immediately assume, however, that a finding of "enrichment" is indicative of a problem. There is a probability that some samples from natural "clean" sediments will contain metals whose concentrations exceed the 95% prediction limit. Interpretation of metal concentrations using these metal to aluminum relationships must also take into consideration sediment grain size, mineralogy, coastal hydrography, and proximity to sources of metals. In the following section are two examples of the use of this metals interpretive tool.

EXAMPLES

The following two examples show how the interpretive tool is used in combination with ancillary information to evaluate metals data from an estuarine system. For the first example, consider the hypothetical situation shown in Figure 15. The estuary has a single major freshwater source, a river entering at its northern end. Hydrographic studies have shown that water circulation in the estuary is to the west-southwest from the mouth of the river and then seaward along the western shore. The estuarine sediment is mostly mud with a strip of fine sand along the shoreline. The

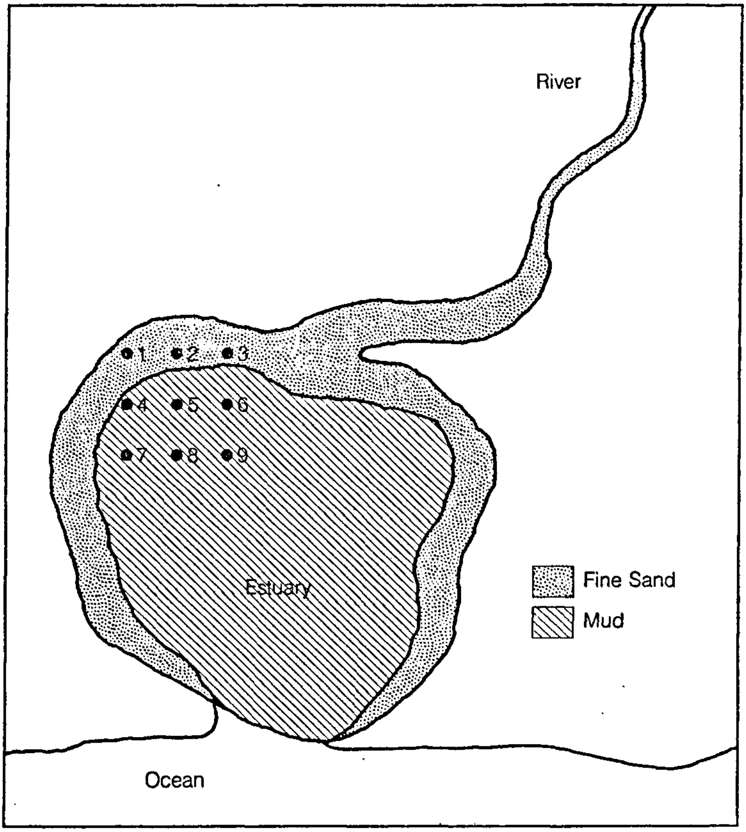

Figure 15. Hypothetical estuary showing sampling stations and sediment grain size.

estuary is still in a "pristine" state with no known anthropogenic sources of metal along its shores or in the river. Sediments from Stations 1 - 9 were collected and analyzed for chromium.

Results of the chromium analyses are shown in Figure 16. Several points are illustrated by these results. Chromium concentrations vary with sediment grain size, being greatest at the stations with finest sediment. However, despite the differences in absolute chromium concentrations, Stations 1, 3, 4, 5, 6 and 8 all have metal values falling within the natural range. Station 2, although statistically enriched with chromium, does not in practice appear indicative of any problem since, it is only slightly above the prediction limit and since the surrounding stations (Sta. 1, 3, 4, 5, 6) all have chromium concentrations within the natural range. Stations 7 and 9 each have chromium values that lie far outside the 95% prediction limit. The chromium value from Station 7 is unusually low which, since the aluminum value is reasonable given the aluminum concentrations of the other similar stations, indicates a possible laboratory error. There are at least three possible explanations for the anomalously high chromium value at Station 9: 1) the sample was contaminated, 2) there was a laboratory error, or 3) there is an unusual and unknown source of chromium in this area. Given the conditions described for this example, the first two possibilities are most likely. To examine these, one needs to review the field data sheets (to identify any field sampling problems), laboratory logbooks, and the original raw data. Occasionally, spurious data from a single replicate can

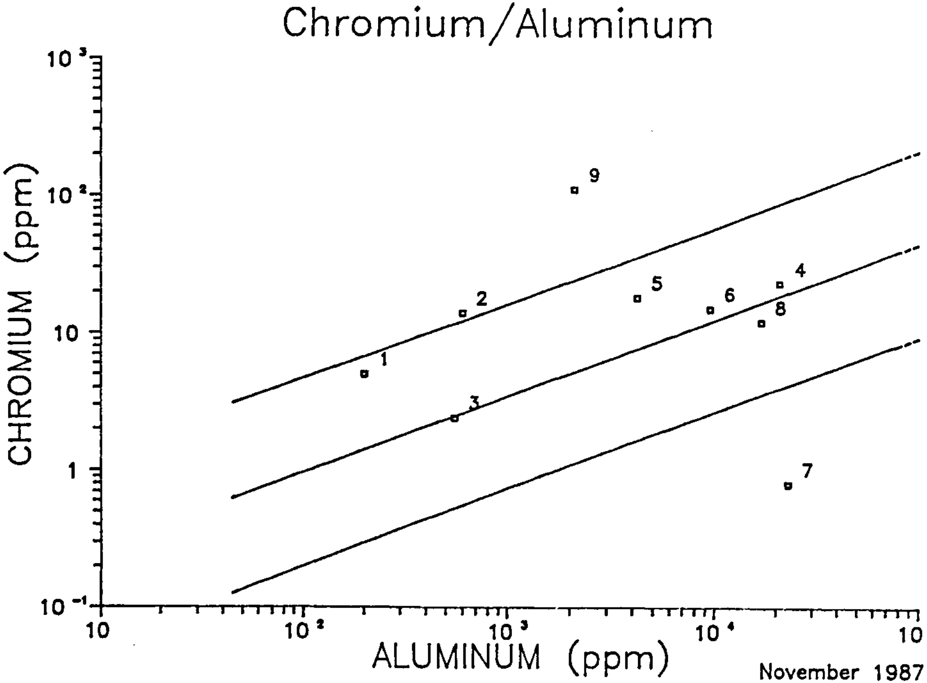

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Figure 16. Chromium results from hypothetical estuarine sampling stations shown in Figure 15.

greatly alter mean concentrations at a site, so the data should be examined for outliers. If the latter two possibilities can be ruled out, then further investigations to determine the source of the chromium are in order.

For the second example, consider the situation shown in Figure 17. Conditions are the same in this hypothetical estuary as they were for the previous example, except for the presence of an urbanized area in the northwest portion of the system. Drainage from the urban area enters the estuary and is a potential source of metal contamination. Sediment samples are taken at the locations indicated and analyzed for chromium; results of the analyses are plotted in Figure 18.

Based on the information described above, the extent of elevated chromium concentrations is indicated by the dashed line in Figure 17. Chromium from the pollution source appears to be accumulating in the sediments at stations 1, 2, and 4. Chromium concentrations at these stations lie outside the 95% confidence interval and, assuming they have been checked for errors, can be considered indicative of chromium-enriched sediment. Stations 3, 5, 6, 7, 8 do not have elevated chromium levels and thus appear to be outside the range of influence of the chromium source. Note that the absolute concentration of chromium at Station 1 is less than that at Stations 5 and 6 but Station 1 is considered to be enriched with chromium. Station 9 has a chromium value just outside the 95% prediction limit but given its location and the metal concentrations at the surrounding stations, the station is judged to be unpolluted.

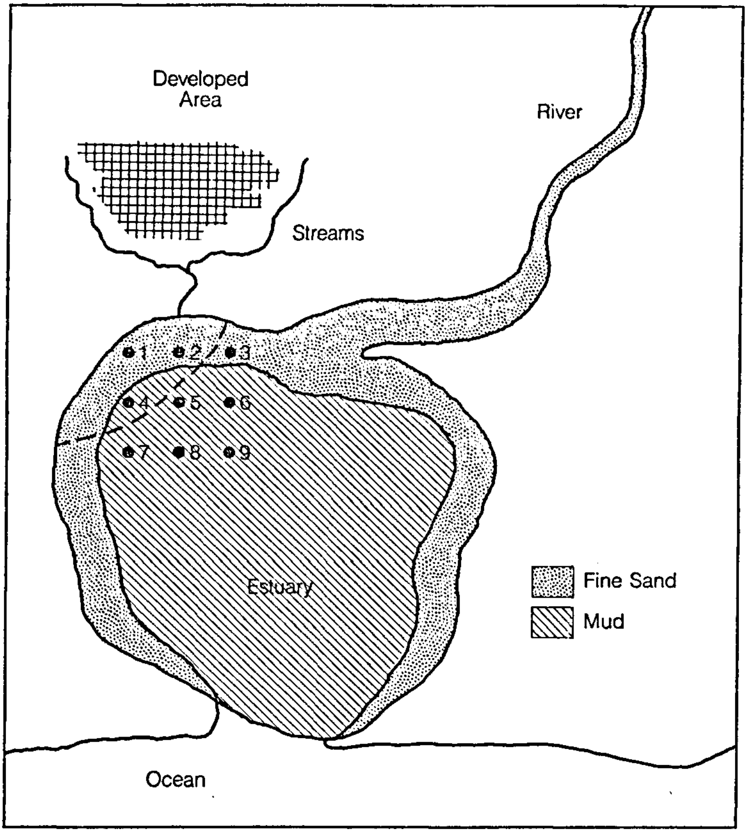

Figure 17. Hypothetical estuary showing metal source, sampling stations, and sediment grain size. Dashed line indicates extent of elevated chromium concentrations.

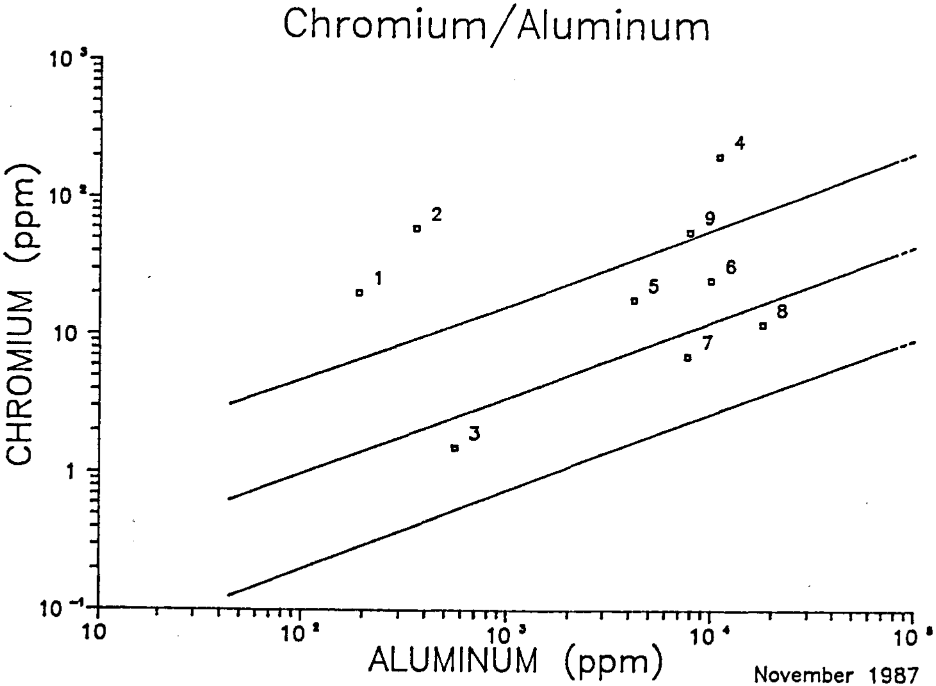

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Figure 18. Chromium results from hypothetical estuarine sampling stations shown in Figure 17.

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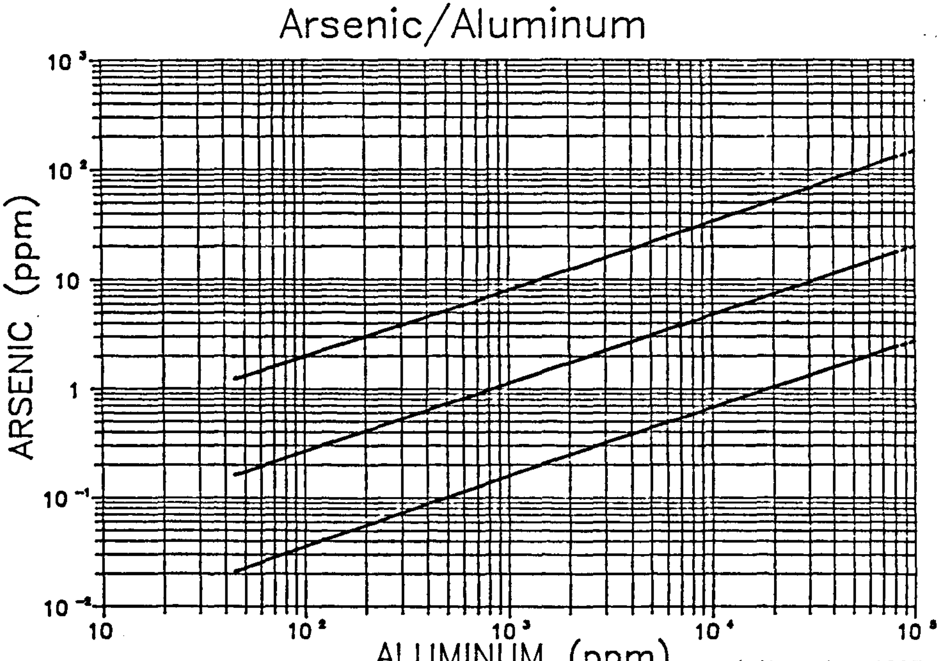
APPENDIX

This appendix contains blank metal/aluminum figures with regression lines and 95% prediction limits. Extrapolated portions of the lines are represented by dashed lines (see explanation in text). Metals data can be plotted on these figures as described in the text for assessment of metal enrichment in estuarine sediments.

Figures



Arsenic/Aluminum

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Figure A1. Arsenic/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

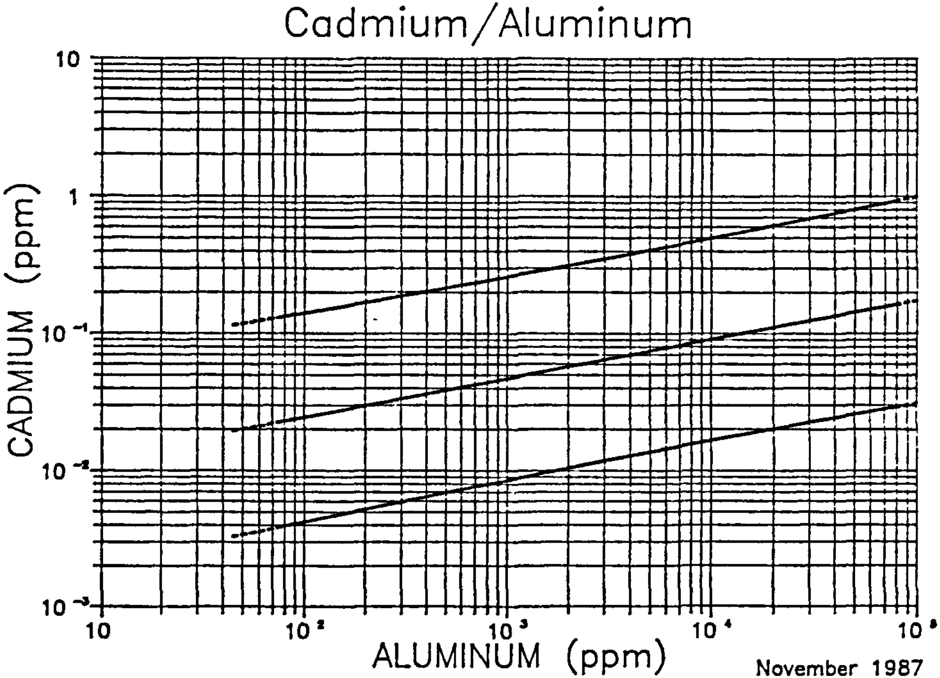

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Figure A2. Cadmium/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

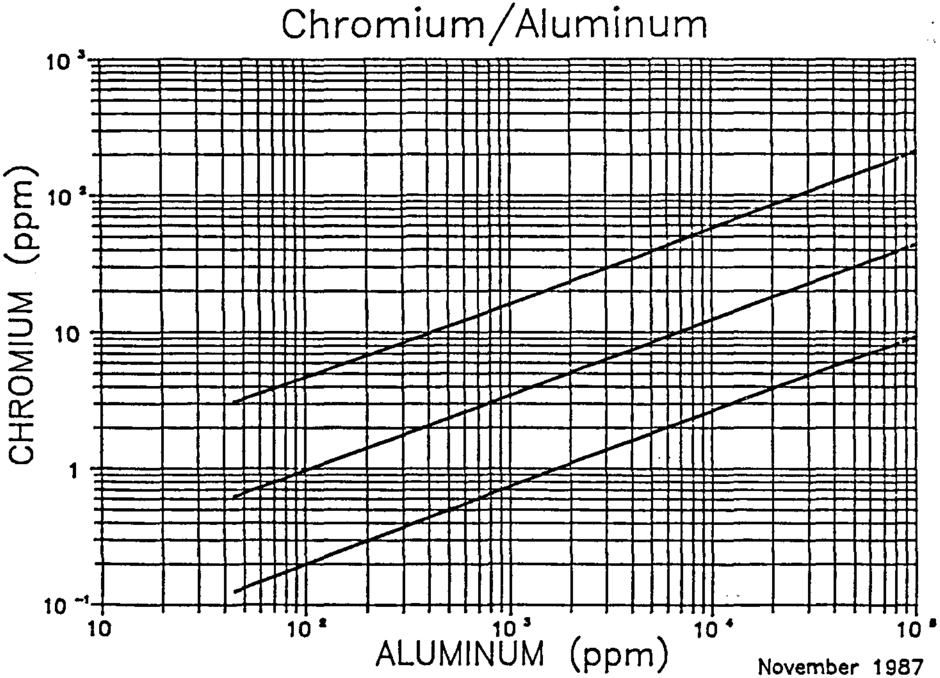

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Figure A3. Chromium/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

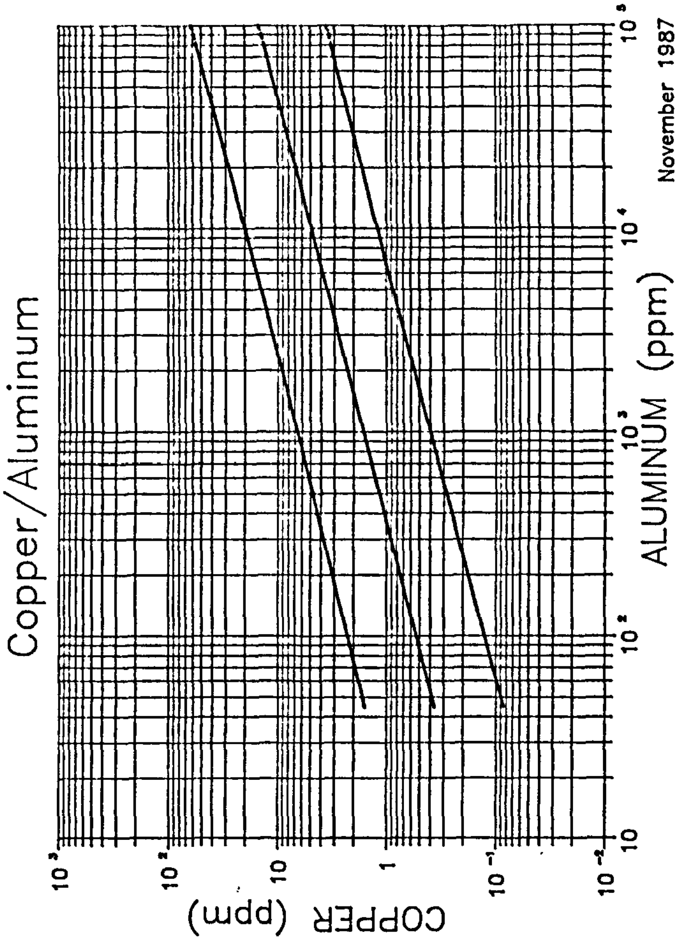

Figure A4. Copper/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

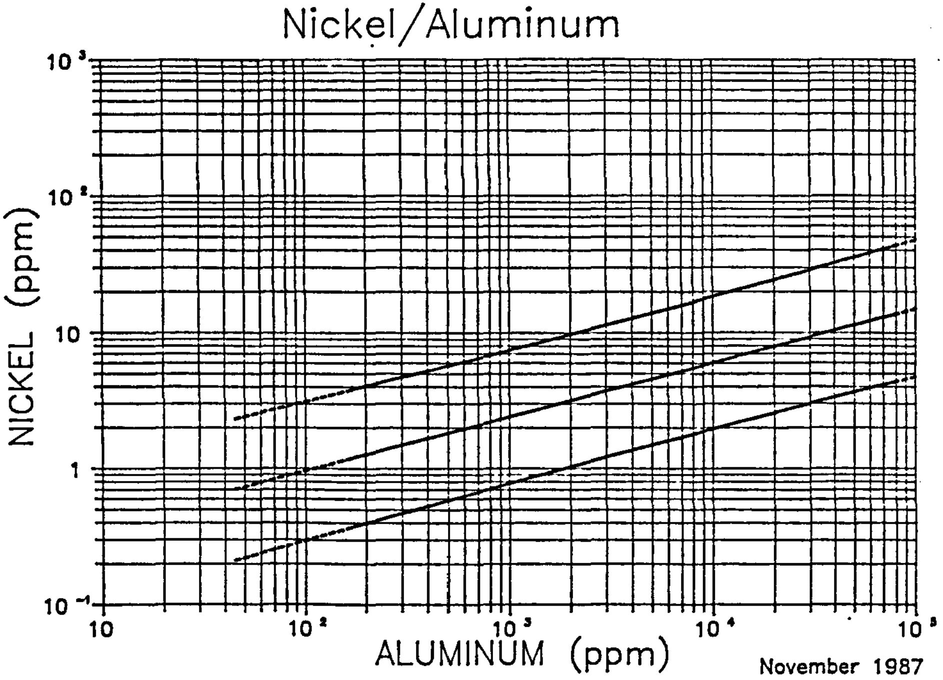

Figure A6. Nickel/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

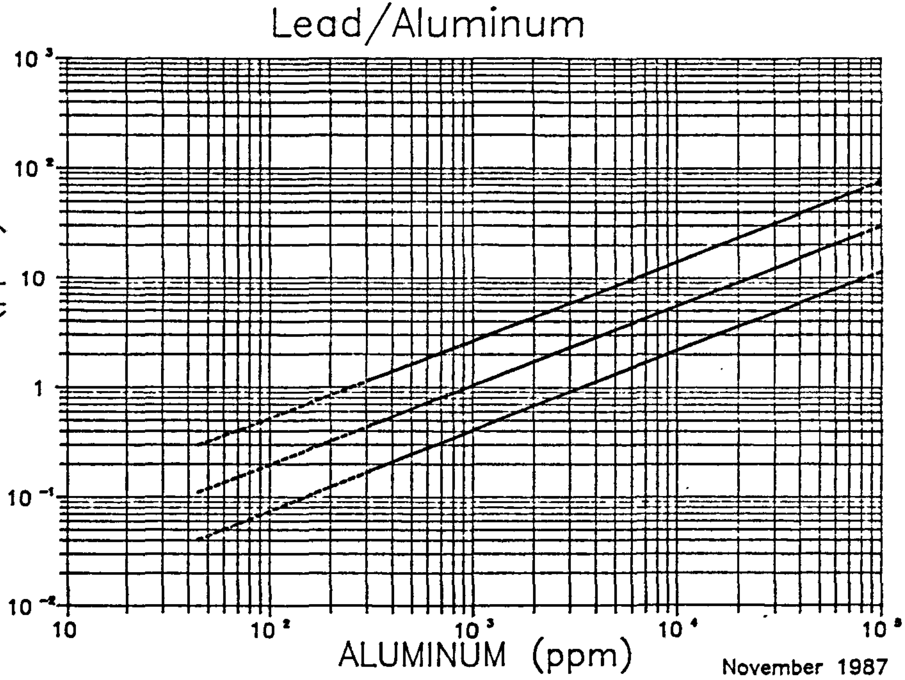

Figure A5. Lead/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

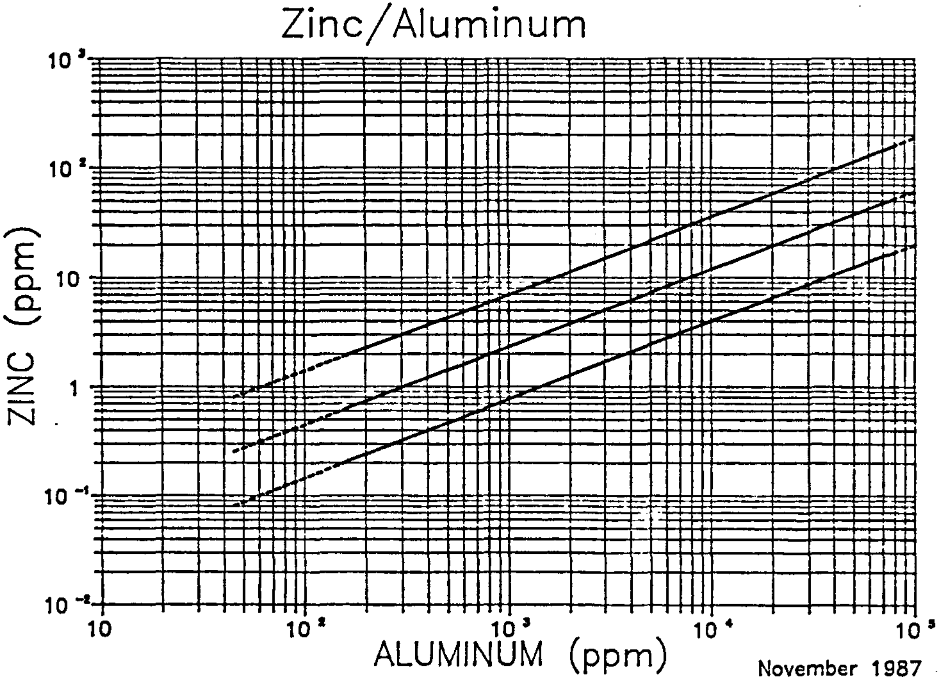

Figure A7. Zinc/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

ANNEX 6

Normalization of heavy metal data by the gradient method

by
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Abstract

When elevated heavy metal concentrations in sediments are only due to a corresponding elevation of the organic matter content the gradient method according to Cato (1977) can facilitate interpretation. The method is based and tested on fine-grained coastal, clastic, surface sediment of similar age and sampled with an even distribution within an area, independent of the exact grain-size distribution. Consequently one is not only refered to samples from pronounced deposition areas. The gradient (inclination coefficient) of the relationship between the metal in question and the organic carbon content is measured using regression analysis. The gradient represents the metal load independent of the variation of the organic matter concentration in the sediments. The steeper gradient, the higher the level of heavy metal contamination, i.e. the more polluted is the sediment. Examples are given from areas along the Swedish west coast of gradients and temporal changes in gradients caused by changes in municipal- and industrial discharges .

Introduction

Awareness of the incorporation into the sediments of heavy metals and persistent organic compounds discharged by man into lakes, rivers and sea has led to the use of sediments as an important tool in assessing the impact of man-made emissions on the environment. Particularly studies of clastic sediments in quiet, coastal and estuarine environments, which geologically have a relatively continuous and rapid rate of deposition, have been found to be useful. Around the world during the two last decades, sediment cores have been used successfully as historical records of the intensified metal pollution. In the same way samples of the topmost sediments have been used to mirror the current level of pollution as well as the dispersion of effluents from industries and municipalities (see reviews in Förstner 1976, 1980, Förstner & Wittmann 1983, Cato 1977).

However, several things may complicate the interpretation of the analytical sediment data and questions which arose early were for example: -How much of the sedimentary metal load is natural and how much is unnatural? - Which samples within a certain area can, considering the range of the analytical values, be considered as unpolluted and which can be considered as polluted? -How to compare heavy metal data from different regimes?

Intepreating sedimentary data is not simple and there has for long existed a demand for simplified interpretation methods, which can be used by others than specialists. Due to this need several normalization techniques have been worked out (recently reviewed by Loring 1988). All with the approachs to eliminate or minimize various natural effects on heavy metal data. Most of them are focused on eliminating the effect caused by grain size variations in the sediment by for example heavy-metal analysis of a specific grain size fraction or by making corrections with reference elements as Al, Fe, Cs, Sc, Li and organic carbon. The success of these normalization techniques have varied depending mainly on the origin of the sediment particles, the organic fraction and type of trace metal. The Li-technique (Loring 1987) and the gradient method treated below for the moment seem to be the most promising of these normalization techniques/methods.

The gradient method was worked out by Cato during the 1970's (Cato 1977) as a consequence of his and others' discovery of the role of organic matter in controlling the heavy metal content of sediments.

Organic matter an important carrier of heavy metals

Of considerable importance in the study of the abundance, distribution, diagenesis and loading of heavy metals is the way in which these elements are held within the sediment (Fig 1). Many dissolved elements are adsorbed or absorbed by organic material (cf. among others Price 1976), dead or alive, and by other suspended particles in the water and sooner or later are deposited and accumulated within the sediment. Besides the direct adsorption of heavy metals on organic and inorganic particles, the metals are presented as sulphides adsorbed and/or coprecipitated by various inorganic and organic precipitates and gels, which exist in the free state or coat the sediment particles. Particularly efficient in the latter process are the hydroxide and hydrated oxide gels and colloids of manganese and iron, which carry a negative charge and attract all cations.

Heavy metals are also included or structurally bound in mineral lattices, but normally to an insignificant level compared to the pollution effects of human activities on the total sediment.

It is obvious from many studies that the organic matter of the sediment plays a great role in the enrichment of trace metals in sedimentary strata. Organic matter and humic acids are effective in absorbing various metal ions by chelation, cation exchange and surface adsorption (e.g. Rashid 1974, Förstner & Wittman 1983). The amount of organic matter in the sediment is in excess compared with the heavy metals, and therefore there exists a strong affinity of the heavy metals for organic matter (i.e. the large surface area), which even results in an immediate adsorption of most, by various early diagenetic processes, mobilized heavy metals (e.g. Håkanson 1973). In general recycling of heavy metals from shelf sediment to the overlying water column can be considered as low due to the excess of binding capacity in the organic fraction of the sediment.

Relationships of heavy metals to organic matter and grain size

As a consequence of this strong affinity of the heavy metals for organic matter many authors have found close, positive, linear, arithmetical, relationships of heavy metals to organic matter or organic carbon with correlationcoefficients varying between 0.5 to 0.95 (Fig. 2; see among others Gorham & Swaine 1965, Piper 1971, Thomas 1972, 1973, Håkanson & Uhrberg 1973, Ryding & Borg 1973, Kuijpers 1974, Clifton & Vivian 1975, Loring 1975, Rust & Waslenchuck 1976, Cato 1977, 1978, 1986a, b, Cato et al. 1980, 1986). In general only a small fraction of the trace metals in clastic sediments were found to be adsorbed by the inorganic particles or present in the interstitial waters . The greater part is associated with the organic matter. However, it must be stressed that contrary results or low correlations also have been reported (e.g. Cranston & Buckley 1972, Landner & Grahn 1975, Förstner & Muller 1974).

Close correlations between trace metals and grain size (Fig. 3) have been found and discussed by many authors (e.g. de Groot et al. 1971, Landner & Grahn 1975, Cato 1977). The relationship increases with decreasing grain size and are in general interpreted as a function of surface adsorption. The surface area increases with the proportion of fine grained particles and also with the amount of organic matter because of its porous nature.

Statistical techniques have been employed by Cato (1977) in an effort to determine whether the clay fraction (<2 um) or the organic matter control the trace metal content of coastal, clastic, sediments along the Swedish coast of the Skagerrak and the Kattegatt. As is decinerable from Table 1, there was a positive relationship of the trace metals to both the clay fraction and the organic carbon fraction, but the former relationships were in general considerably weaker than the latter.

The weaker relationship of the trace metals to the clay fraction was interpreted by Cato (op. cit) as a secondary phenomenon as a consequence of the strong and positive relationship of organic matter to the clay fraction (correlation coefficients 0.62 - 0.7). The latter relationship was due to the fact that both clay particles and organic matter are primaraly deposited in quiet and sheltered environments, i.e. the deposition is a function of the sedimentary environment.

From above we may understand that elevated concentrations of heavy metals are mainly due to elevated concentrations of organic matter. Therefore, direct comparison of trace metal data is normally not possible without prior normalization of the differences in binding capacity of the sediment, i.e. the organic matter content.

The strength of the relationships of heavy metals to organic carbon due to the correlation coefficients (r^2) was generally in the order Cd>Zn>Cu>Hg>Ni>Pb>V in the Kattegatt and Skagerrak coastal sediments, but variations existed mainly due to changed position of Ni in the order (Cato 1977). The order was similar to that found by Rashid (1974) of the preferential absorption of some trace metals to organic matter. Rashid interpreated his results as a function of the degree of selectivity in the relation of various metal ions in the macromolecules of humic acids.

The heavy effluents discharged from a treatment plant, south of Gothenburg, Sweden) during the years 1952-74 transformed the Välen estuary into a highly contaminated area, with very high concentrations of organic matter and high concentrations of several, very toxic, heavy metals. The correspondence between the high metal contents and the high C/N ratios justified the assumption that the heavy metals originate from the allochthonous organic matter (sludge products) directly derived from the treatment plant.

A similar assumption, but in this case concerning wood fibres, was made by Loring (1975) when he obtained a highly positive correlation (r=0.72) in the relationship between the mercury content and the C/N ratios in Saguenay Fjord sediments. High metal content in the sediments due to municipal sewer outfalls and sludge dumping have been reported by several authors (among others Klein & Goldberg 1970, Appelquist et al. 1972, Clifton & Vivian 1975). In these cases the heavy metals were associated with the organic matter and deposited with it.

All these studies show that heavy metals are mainly associated with the organic matter both in uncontaminated and contaminated sediments of clastic origin. The relationships were found by Cato (1977) to be considerably stronger in the contaminated areas than in the uncontaminated areas. He interpreated this as a probable consequence of the fact that the modes of transport and deposition of the elements from the effluents were the same, since the elements are mainly held in the discharged sludge products and consequently settled with them.

Determination of the heavy metal load

The statistical relationships of the heavy metals to both chemical and physical properties are of considerable importance in attempts to make comparisons with other regimes or different parts of an area, as well as a statement of the total load of heavy metals in the area in question. The relationship between the two parameters y and x in surface sediment (in this case heavy metals and organic carbon respectively) may be an important indication of a divergence due to contamination. The dispersion or systematical divergence in correlation diagrams of one or more data pairs (x/y values) from previously known natural linear relationships of uncontaminated regimes very often clearly reveals an existing contamination and the degree of pollution (Fig. 4). The diverging values from the contaminated Välen estuary and Askimsviken Bay (Fig. 5) was found by Cato (1977) to follow relationships determined by increased gradients (inclination coefficients) of each heavy metal compared to the corresponding gradients of the linear and arithmetical relationships of the natural load of the same metals of an uncontaminated area of the Swedish west coast (Fig. 6).

Since in general the small differences in the intercept ("b", see below) between relationships from different regimes can be interpreted as a function of the amount of heavy metals held within the mineral lattices or coprecipitated to the inorganic grains by various Fe/Mn hydroxides and hydrated oxides, Cato (1977) proposed that the metal load or the degree of contamination for a certain metal of a certain area easiest can be described by only the inclination coefficient (the gradient) of the regression analysis, i.e. the slope "a" of the equation $y = ax + b$ between metal contents and organic carbon contents of the sediment. The principles are shown in Figure 7.

From the figure we may understand that a heavy metal value itself does not say anything about the environmental load of the sediment, if the value can not be related to a natural "background" gradient of the relationship between the heavy metal in question and the organic matter. To achieve a correct conclusion of the heavy metal load of a certain area, the gradient of the area has to be determined and compared with a natural "background" gradient from an uncontaminated area.

Within a limited coastal area one may have different gradients due to differences in the pollution load between different regimes of the area. Therefore it is important to find out strongly diverging data pairs in a plot and derivate their geographical origin. Such data should be excluded in the regression analysis. This is necessary in order to avoid a "false" regression line and a "false" correlation coefficient, since a few data pairs showing a strong divergence may rule the regression line and give rise to a gradient which is not representative of the main part of the data (cf. Walker 1950, pp. 237-239). When such diverging data can be derivated to a specific regime the load of the latter can be determined by a separate regression analysis (Figs. 6 and 8).

Applications to the gradient method

In Figures 9-15 heavy metal concentrations of Hg, Pb, Cu, Ni, Zn, Cd and V versus organic carbon concentrations from different regimes of the Skagerrak and Kattegatt have been treated according to the above mentioned gradient method. The analytical data are taken from the following investigations:

* Idefjorden: Olausson (1975a); Olausson & Engvall (unpubl.)
* Kattegatt: Olausson (1975a)
* Skagerrak: Olausson (1975a)
* Byfjorden: Olausson (1975b); Olausson (unpubl.)
* Fjords of Orust and Tjörn: Olausson (1975a), Cato (1983)
* Brofjorden: Cato (1977), Cato et al. (1986)
* Välen: Cato (1977)
* Askimsviken: Cato et al. (1978)
* Gullmarsfjorden: Joslin (1982)
* Gothenburg Archipelago: Cato (1986a)
* Stenungsund: Edgren (1975, 1978), Gustavsson (1982), Cato (1986b)

The gradient method identifies Idefjorden, Stenungsund and, prior to 1974 the Välen estuary, as the most metal (except Ni) contaminated areas known along the Swedish west coast. With respect to Hg and Cd, even the Gothenburg Archipelago should be included in this seriously loaded group of areas. Byfjorden and Askimsviken Bay are two other contaminated coastal areas, while the other areas studied here generally show a minor pollution, in some cases close to the natural background (e.g. Brofjorden 1972). However, the Gullmarsfjorden is evidently loaded with respect to Ni.

In Välen, Stenungsund and Brofjorden the investigations have been repeated with some years interval in order to clarify the development with respect to the heavy metal load.

The recovery of the prior to 1974 highly polluted Välen estuary has been studied in detail after the drastically abatement in December 1974, when the treatment plant was closed down (Cato et al. 1980). The recovery process was clearly indicated by a decreasing gradient of the heavy metal load (Figs. 9-15) accompanied by the succession in macro- and meiobenthic communities up to 1977 (op.cit.).

In the Stenungsund area, surrounded by various petrochemical industries, the heavy metal load of the sediments has been studied at three occasions between 1975 and 1985 (Cato 1986b). The metal gradients of Stenungsund show beyond doubt that the area is loaded with respect to Cu, Pb and V. However, the trends of Pb and Cu are decreasing compared with 1981 and earlier. The situation for Cd is reversed.

Prior to 1975 the Brofjorden area was considered as an uncontaminated regime of the Swedish west coast according to the basic investigations conducted in 1972 (Cato 1977). In order to clarify the changes that may have taken place as a consequence of the building of an oil refinery in the fjord in 1975 the area was again studied in 1984 (Cato et al. 1986). The metal gradients showed that the V, Pb, Cd and Zn loads had increased between 1972 and 1984, while the Cu and Ni loads were on the whole unchanged.

From above we have seen heavy-metal gradients change in three different areas studied during a period of about one decade. The changes are analogous with the development in each area respectively. In the Välen estuary the gradients decreased due to the abatement of the waste-water discharge, in Stenungsund the same succession was observed due to a better treatment of the industrial spill-water, while in Brofjorden the reversed succession was observed due to the industrialization of the area.

In order to achieve objectivity and to eliminate the natural variations of heavy metals due to the various amount of organic matter in coastal and estuarine sediments the above mentioned examples show the advantage and also possibility to treat and interpret metal data from such regions by using the "gradient method". Wheather this normalization technique works outside areas with postglacial, clastic, marine sediments has not yet been tested, but several facts suggest that it may not apply to carbonate sediments.

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Table 1. Correlation coefficients of the relationships of heavy metals to organic carbon and to the clay fraction (<2um) in sediments from three different areas of the Swedish west coast. The correlation coefficients of the clay fraction to organic carbon are also given.

	Brofjorden				Välen		Gothenburg Archipelago	
	1972 n=57-62		1984 n=17		1973 n=20-28		1982 n=26-32	
	org C	<2um	org C	<2um	org C	<2um	org C	<2um
Zn	0.85	0.52	0.90	0.16	0.82	0.64	0.76	0.45
Cu	0.70	0.59	0.74	0.06	0.78	0.45	0.65	0.20
Hg	0.51	0.47	n.d.	n.d.	0.75	0.49	0.65	0.36
Ni	0.51	0.51	0.45	0.24	0.93	0.83	0.57	0.57
Pb	0.34	0.28	0.66	0.32	0.74	0.30	0.23	0.01
Cd	0.93	n.d.	0.92	0.10	n.d.	n.d.	0.61	0.29
V	0.30	n.d.	0.49	0.14	n.d.	n.d.	n.d.	n.d.
org C	-	0.62	-	0.52	-	0.70	-	0.38

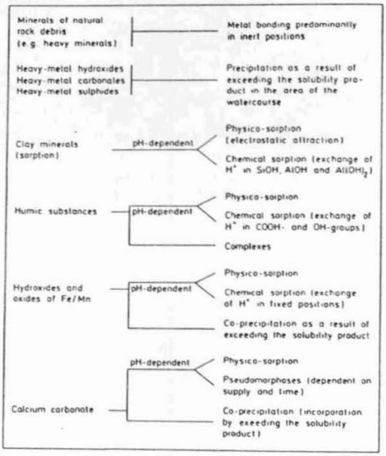

Fig. 1. Carrier substances and mechanisms of heavy-metal bonding (after Förstner & Patchineelam 1976)

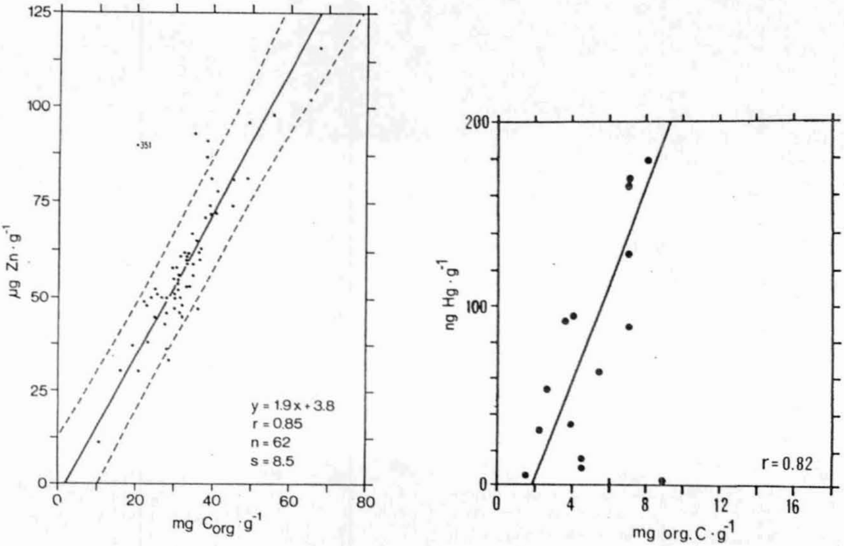

Fig. 2. Relationships between zinc and organic carbon (right) and between mercury and organic carbon (left) of the clayey and silty surficial sediments of Brofjorden and Askimsviken Bay respectively. The dashed lines denote the 95% confidence interval (from Cato 1977 and Cato et al. 1978).

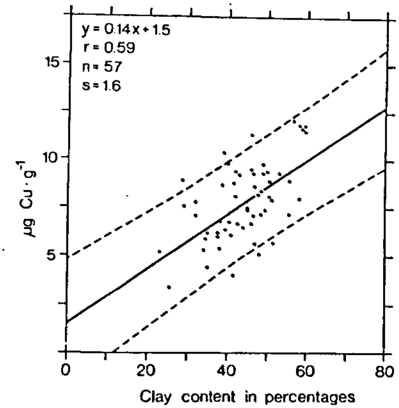

Fig. 3. Relationship between copper and the clay fraction in the surficial sediments of Brofjorden. The dashed lines denote the 95% confidence interval (from Cato 1977).

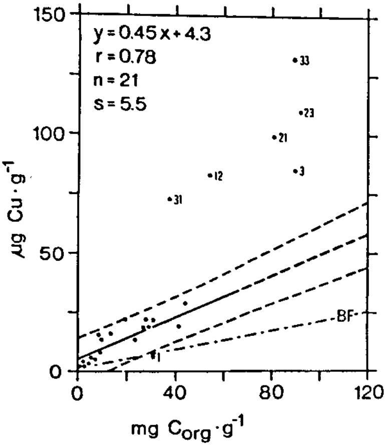

Fig. 4. Relationship between copper and organic carbon in the surfical sediments of the Välen estuary and Askimsviken Bay in 1973. The regression line (continuous line) gives the relation in the lower Välen estuary and Askimsviken Bay. The dashed lines denote the 95% confidence interval. The line of dots and dashes marked BF refers to the natural background regression line of the uncontaminated Brofjorden in 1972. Note the great divergence of the values (marked with site numbers) from the upper Välen estuary, which is heavily contaminated (from Cato 1977).

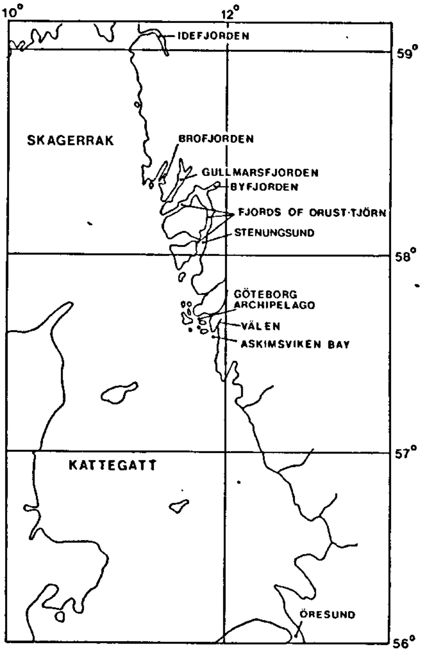

Fig. 5. Outline map of the Kattegatt and Skagerrak areas, showing the location of the areas mentioned in the text.

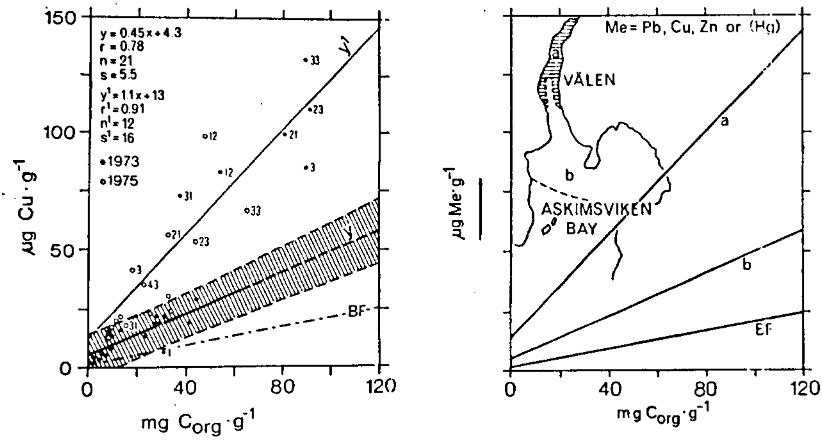

Fig. 6. Relationship between copper and organic carbon in the surficial sediments of the Välen estuary and Askimsviken Bay in 1973 (solid circles) and the Välen estuary in 1975 (open circles). The regression line (y) gives the relation in 1973 in the lower Välen estuary and Askimsviken Bay and the line (y^1) gives the relation in the upper Välen estuary in 1973 and 1975. The hatched area denotes the 95% confidenceinterval of the regression line (y). The line of dots and dashes marked BF refers to the background gradient of the uncontaminated Brofjorden in 1972. The principles are shown in the generalized summary diagram (left) (from Cato 1977).

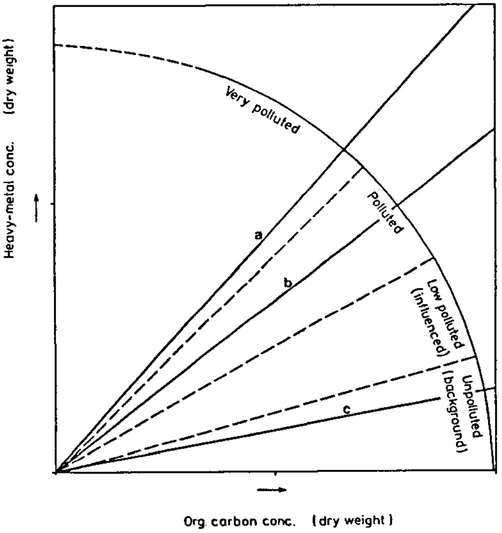

Fig. 7. The heavy-metal load or the degree (gradient) of contamination in sediments according to Cato (1977). The load is illustrated by the inclination coefficient of the relationship between the metal in question and organic carbon. The degree of contamination increases with increasing inclination coefficient, i.e. case "a" is more contaminated than the cases "b" and "c" (from Cato 1986).

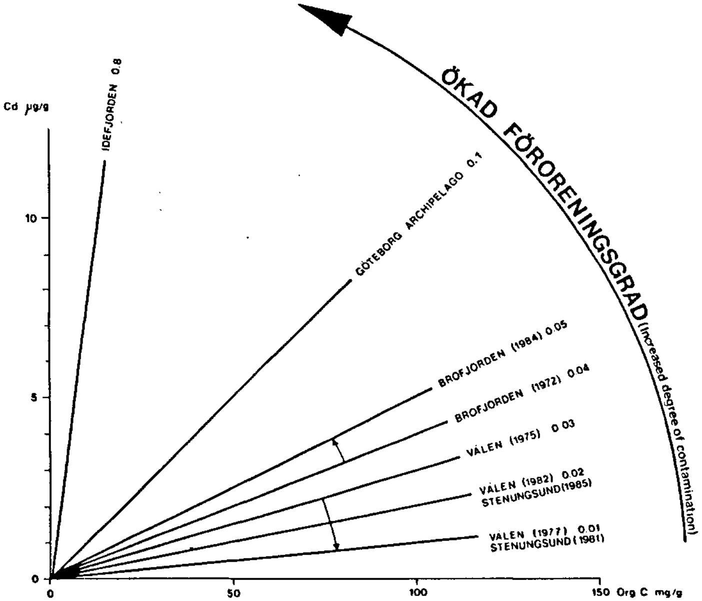

Fig. 8. The cadmium load or the degree (gradient) of cadmium contamination in the surficial sediments of some areas along the Swedish west coast at various dates. The load is illustrated by the inclination coefficient of the relationship between cadmium and organic carbon, according to the gradient method (Cato 1977). The degree of contamination increases with increasing inclination coefficient, i.e. Idefjorden is much more contaminated that e.g Brofjorden. The arrows show temporal changes in gradients caused by changes in municipal and/or industrial discharges.

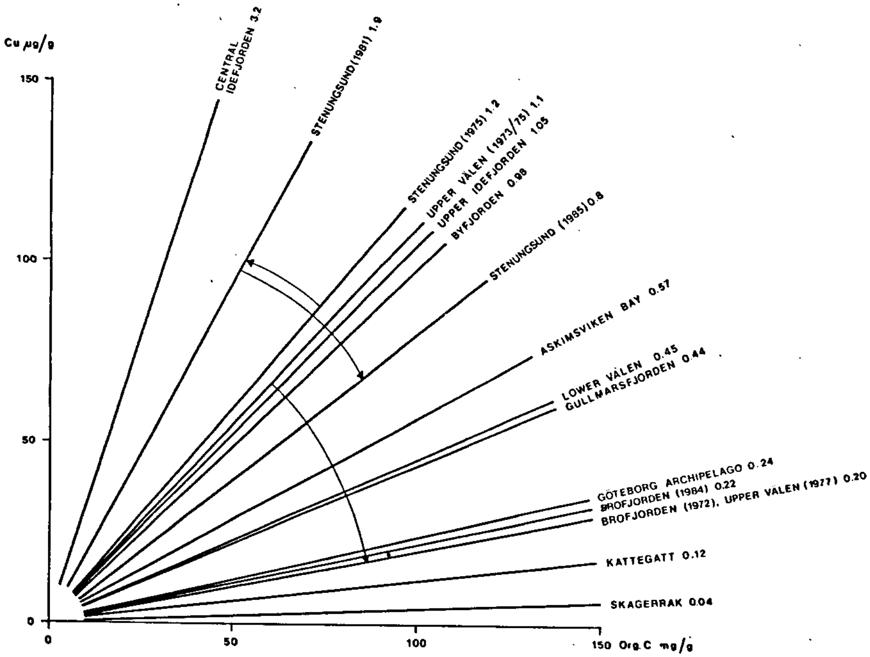

Fig. 9. The copper load or the degree of copper contamination in surficial sediments from some areas along the Swedish west coast. For further explanation, see figure 8.

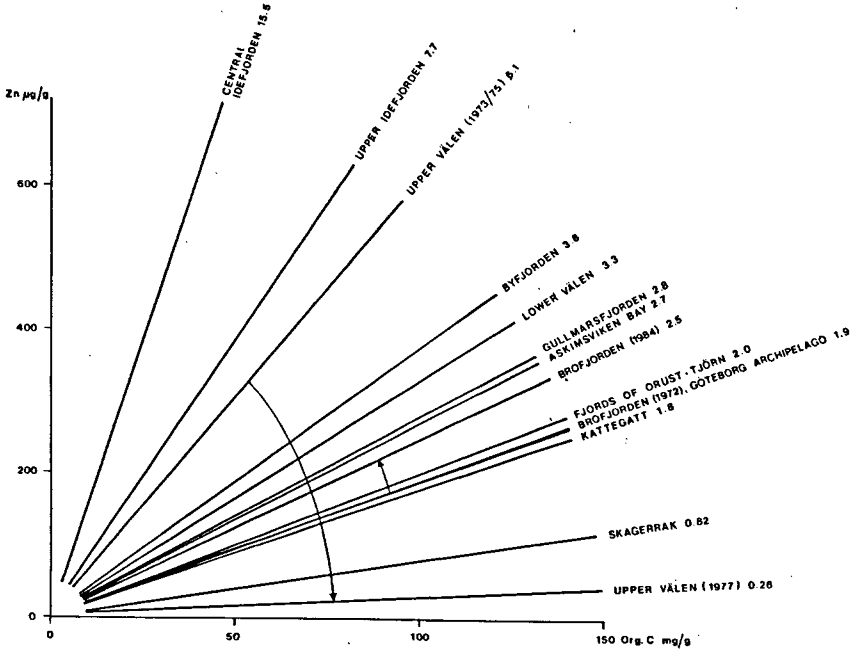

Fig. 10. The zinc load or the degree of zinc contamination in surficial sediments from some areas along the Swedish west coast. For further explanation, see figure 8.

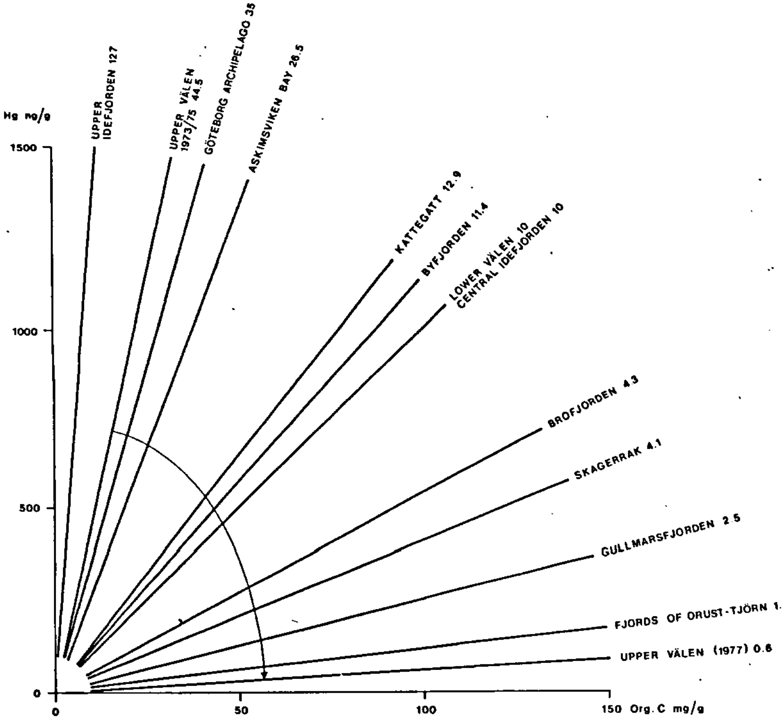

Fig. 11. The mercury load or the degree of mercury contamination in surficial sediments from some areas along the Swedish west coast. For further explanation, see figure 8.

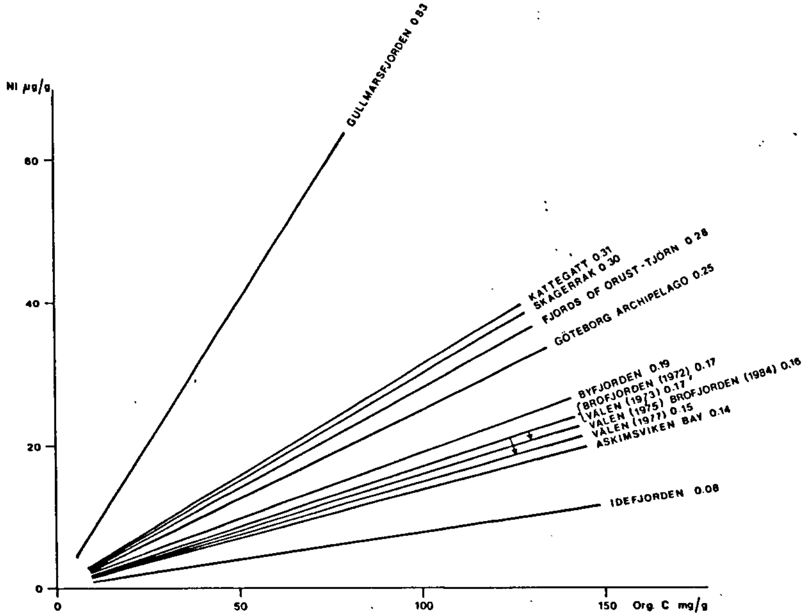

Fig. 12. The Nickel load or the degree of nickel contamination in the surficial sediments from some areas along the Swedish west coast. For further explanation, see figure 8.

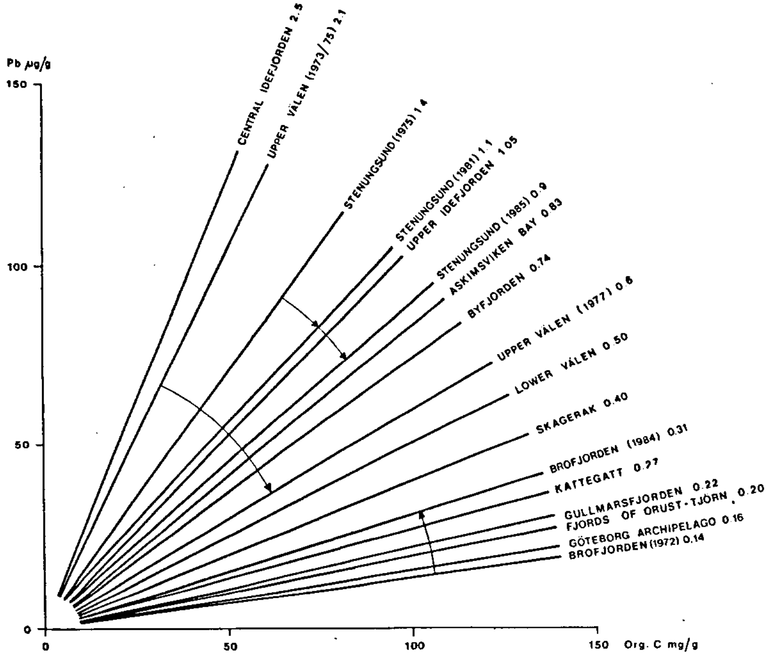

Fig. 13. The lead load or the degree of lead contamination in surficial sediments from some areas along the Swedish west coast. For further explanation, see figure 8.

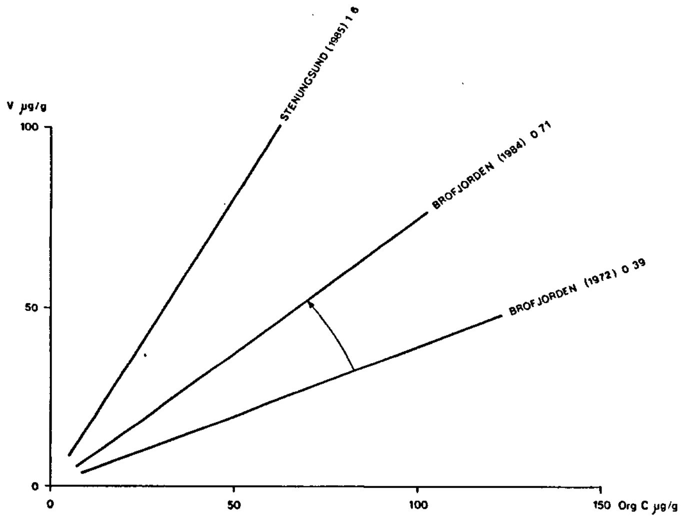

Fig. 14. The vanadium load or the degree of vanadium contamination in surficial sediments from some areas along the Swedish west coast. For further explanation, see figure 8.

ANNEX 7

PROTOCOL FOR INTERCOMPARISON EXERCISE ON TRACE METALS IN SUSPENDED PARTICULATE MATTER (SPM)

Introduction

To study contaminant fluxes in the marine environment, especially those between river mouths and offshore areas, it is essential to know, for instance, the mass per volume, density, grain size spectra, and chemical composition of the suspended particulate matter (SPM). For the understanding of biotic and sedimentary fluxes, it is important to distinguish between contaminants in the particulate and the dissolved phase.

In addition, a substantial amount of contaminants, especially in the case of trace metals, is discharged into rivers and estuaries in a particulate form (e.g., industrial wastes, dredged material). In most studies, filtration procedures are used for collecting SPM. Generally, the filtration results in only small quantities (a few mg) of SPM samples. Thus, analytical treatment for trace metal determinations requires well-experienced laboratories, sensitive detection methods and rigorous quality assurance measures. This includes the participation in intercomparison exercises organized in a proper way.

According to the responses to a questionnaire submitted to ICES in August 1986, 60 laboratories are favorable towards participation in an intercomparison exercise (Annex 9, C.M.1988/E:25). Such an exercise seems feasible and could be carried out in stages.

Objectives of the Intercomparison Exercise (Stage 1)

Studies of particulate matter in seawater involve water sampling, particulate matter recovery (filtration or centrifugation) and chemical analyses. Stage 1 of the intercomparison exercise is defined as the analytical exercise and the objective is to evaluate the possibilities and capabilities of the laboratories to analyze small samples (1-5 mg) accurately and reproducibly.

Working Procedure

Each laboratory who plans to participate in the intercomparison exercise will be expected to perform a preliminary exercise:

i) Use a standard sediment reference material (free choice) certified for trace metals or any other well characterized material (i.e., ICES intercomparison samples, internal laboratory standards, etc.).

ii) Weigh out a minimum of three subsamples in the range 1-5 mg and analyze them for the metals for which certified or accepted values exist.

iii) Once the laboratory has achieved the ability to analyze the small samples, they should notify the coordinator and request the intercomparison material. The latest date for requesting the material is 30 June 1989.

Following the preliminary exercise described above, the laboratory notifies the organizer about their desire for further participation. The laboratory will then receive 3 vials with different homogenized certified reference material, containing approximately 5 mg, 15 mg, and 20 mg, respectively. The laboratory is asked to subsample 3 replicates from each vial with sample weights approximately 1 mg, 3 mg, and 5 mg respectively. All the replicates (a total of 9) are analyzed for Cu, Pb, Zn, Cd, Al, Li, Fe, Mn, Ni and Cr. The method described by the WGMS (total dissolution using HF, see Loring and Rantala, 1989) is recommended.

Time Schedule

The Norwegian Institute for Water Research (NIVA) in Oslo has agreed to organize stage 1 of the exercise.

The following timetable will be followed:

Feb 1989:	Preparation of the protocol (this document).
Mar 1989:	A letter of invitation including this protocol is distributed to the 60 laboratories originally interested. The laboratories are asked to perform a preliminary test on analyses of small sample quantities.
Apr 1989:	Review of the protocol by WGSATM and if necessary the distribution of the revised version to the potential participants.
Jun 1989:	The participants notify the organizer (NIVA) regarding the decision made based on the preliminary test.
Jul 1989:	Preparation of samples for distribution.
Aug 1989:	Distribution of samples.
Dec 1989:	Receipt of results by organizer.
Jan-Feb 1990:	Assessment of results and presentation of draft report to the WGMS annual meeting.

Reference

Loring, D.H. and Rantala, R.T.T., 1989. Total and partial method of digestion for estuarine and coastal sediments and suspended particulate matter. ICES Techniques in Marine Environmental Sciences.

ANNEX 8

Blood-groups in society in relation to issues concerning environmental pollution.

	aim	function
Scientists	to study processes in order to understand the physical and chemical environment.	'give warnings' 'give advice'
Public	to be interested in its environment and its health.	'express concern' 'demand action'
Politicians	to take away public concern by formulating a policy	'take decisions' 'issue laws' 'provide money'
Management	to reach the goals formulated by politicians	'steering' 'monitoring' 'checking'

ANNEX 9

PROCEDURE AND CRITERIA FOR THE SELECTION OF DREDGED MATERIAL FROM DUTCH HARBOURS FOR DISPOSAL AT SEA

50 million cubic meters of mud and sand are dredged each year in harbors along the Dutch coast. Most of this (about 40%) originates in the Rotterdam area. In the past this dredged material was put on land or dumped at sea. However, the material appeared to be polluted and a growing awareness of the risks for the environment led to a reduction of the dumping of polluted dredging material in the sea. Instead, it is put in dumps with facilities to prevent contamination of the environment. At the moment, about 40% of the material from Rotterdam is stored there, primarily the most polluted up-river mud. The rest, consisting mainly of freshly sedimented North Sea mud and sand, is still dumped at sea. A geographic boundary discriminates the two types of dredged material.

The Netherlands policy is to reduce the pollution of the environment (including the North Sea) and promises were made last year in international talks on pollution of the Rhine and North Sea (the International Rhine Commission and the International Conference on the Protection of the North Sea) that loads of polluting substances to the Rhine and the North Sea will be reduced by at least 50% by 1995.

The department in control of the North Sea (RWS, North Sea Directorate) designed a scheme for dredged material to realize this goal. The scheme provides a stepwise reduction of the loads of dredged material to zero in the near future. By then, all dredging material is expected to have a near "natural" quality so that it can be disposed in the sea without special precautions. A large dump in the Rotterdam area, constructed in 1987, which stores 150 million cubic meters, plays an important role in this scheme.

In order to control the loads of polluting substances that go to the sea with the dredged material, it is essential to have a selection system which is based on the quality and the quantity of pollutants in the dredged material and on the impact of the dumping on the sediments of the receiving water system.

The requirements for this selection system are:

- the quality and quantity of pollutants in dredged material disposed in the sea in 1986 should not be exceeded;
- it should be applicable in all Dutch harbors;
- it should lead to an improvement of the quality of dredged material;
- it should take into account the capacity of the recently constructed dump (150 million cubic meters).

These requirements were met by calculating criteria for quality and quantity as follows:

- a data set was created containing the quality of dredged material disposed in the sea in 1986 from all sections of the Dutch coast;
- the amounts of dredged material from all harbors involved in 1986 were determined;
- the data on quality were normalized according to the Dutch procedure, which is described below;
- the highest values were selected and called the Allowed Maximum Values;
- the anthropogenic loads for 1986 were calculated by subtracting the Reference Values (Table 3), adjusted for sediment composition as described below, from the total concentration to determine the Allowed Maximum Anthropogenic Load Values.

Tables 1 and 2 present the calculated criteria. A Reference Value was defined for Dutch soils of standard composition (see Table 3). The standard composition is 25% lutum (< 2 µm fraction) and 10% organic matter.

To correct a measured value (Me:meas) in a non-standard soil to a standardized value (Me:st) in standard soil, the formulae (Form) of Table 3 are used:

$$Me{:}st = Me{:}meas * (Form{:}st/Form{:}meas)$$

These criteria will be applied to dredged material that arises in Dutch harbors. The dredged material that does not meet these criteria is put in the depot dump. The on-going improvements of sediment quality assures an end to use of depot dumps.

Reference values for multifunctional soils. These reference values are valid for soils of standard composition (25% lutum and 10% organic matter).

Table 1 The Allowed Maximum Values of pollutants for mud from dredging compartments of harbours along the dutch coast.

Pollutant	mg/kg
Zinc	365
Copper	58
Chromium	120
Lead	110
Cadmium	1.7
Nickel	40
Mercury	1.5
Arsenic	37
Naphthalene	1.10
Phenanthrene	.90
Anthracene	.45
Fluoranthene	3.20
Chrysene	1.35
Benzo(a)anthracene	1.50
Benzo(a)pyrene	1.50
Benzo(k)fluoranthene	10.5
Indeno(123,cd)pyrene	10.5
Benzo(ghi)perylene	10.5
Benzo(b)fluoranthene	10.5
Extractable-organic-chloride	7.0
Oil	2000

All other organic micro-pollutants are not allowed to exceed Reference Values of The Multifunctional Sediment

Table 2. The allowed maximum yearly load of pollutants in dredged material of 4 harbours along the dutch coast that is to be disposed in the North Sea

		Rot-terdam	Scheve-ningen	IJ-muiden	Eems haven
Zinc	(Mg)	270	10	-	-
Cadmium	(Kg)	1200	25	-	-
Mercury	(Kg)	400	40	320	25
Naptalene	(Kg)	70	-	25	-
Fluoranthene	(Kg)	230	-	500	7
Chrysene	(Kg)	60	-	30	6
Benz(a)pyrene	(Kg)	-	-	130	-
Oil	(Mg)	1200	60	650	10
Extr.org.Cl	(Kg)	4000	70	-	70

A - indicates that anthropogenic loads are not allowed. Anthropogenic loads of all other pollutants are not allowed.

Table 3. Refefence values of the Multifunctional Sediment at standard sediment consisting of 25 % Lutum (L) and 10 % organic material (H).
Source: Milieu Programma 1988-1991, Voortgangsrapport.

	Formula		Reference value (mg/kg)
Zinc	50 + 1.5 * (2 * L + H)		140
Copper	15 + .6 * (L + H)		36
Chromium	50 + 2 * L		100
Lead	50 + L + H		85
Cadmium	.4 + .007 * (L + 3 * H)		.8
Nickel	10 + L		35
Mercury	.2 + .0017 * (2 * L + H)		.3
Arsenic	15 + .4 * (L + H)		29
		2 < H < 30	
PCB IUPAC nr 28	.001 * H / 10	,,	.001*
PCB IUPAC nr 52	,,	,,	.001*
Hexachlorocyclohexane	,,	,,	.001*
Endrin	,,	,,	.001*
Tetracloroethane	,,	,,	.001*
Tetrachloromethane	,,	,,	.001*
Trichloroethane	,,	,,	.001*
Trichloroethene	,,	,,	.001*
Trichloromethane	,,	,,	.001*
Naphthalene	.01 * H / 10	,,	.01
Chrysene	,,	,,	.01
PCB IUPAC nr 101	,,	,,	.01
PCB IUPAC nr 118	,,	,,	.01
PCB IUPAC nr 138	,,	,,	.01
PCB IUPAC nr 153	,,	,,	.01
PCB IUPAC nr 180	,,	,,	.01
Chloropropene	,,	,,	.01
Tetrachloroethene	,,	,,	.01
Hexachloroethane	,,	,,	.01
Hexeachlorobutadiene	,,	,,	.01
Heptachlorepoxide	,,	,,	.01
Dichlorobenzene	,,	,,	.01
Trichlorobenzene	,,	,,	.01
Tetrachlorobenzene	,,	,,	.01
Hexachlorobenzene	,,	,,	.01
Monochloronitrobenzene	,,	,,	.01
Dichloronitrobenzene	,,	,,	.01
Aldrin	,,	,,	.01
Dieldrin	,,	,,	.01
Chlordan	,,	,,	.01
Endosulfan	,,	,,	.01
Trifluralin	,,	,,	.01
Azinphos-methyl	,,	,,	.01
Azinphos-ethyl	,,	,,	.01
Parathion	,,	,,	.01
Parathionmethyl	,,	,,	.01
Disulfoton	,,	,,	.01
Fenitrothion	,,	,,	.01
Triazofos	,,	,,	.01
Phenanthrene	.10 * H / 10	,,	.10
Anthracene	,,	,,	.10
Fluoranthene	,,	,,	.10
Benzo(a)pyrene	,,	,,	.10
DDD	,,	,,	.10
DDE	,,	,,	.10
Pentachlorophenol	,,	,,	.10
Octane	1.0 * H / 10	,,	1.0
Heptane	,,	,,	1.0
Benzo(a)anthracene	,,	,,	1.0
Benzo(k)fluoranthene	10 * H / 10	,,	10
Indeno(123,cd)pyrene	,,	,,	10
Benzo(ghi)perylene	,,	,,	10
Oil	50 * H / 10	,,	50

*:or detection limit when higher then the indicated value

ANNEX 10

TECH NOTES

May 1987

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APPARENT EFFECTS THRESHOLDS — AET

What is an AET?

An AET, or Apparent Effects Threshold, is the sediment concentration of a contaminant above which adverse biological effects are always expected to occur. The AET approach does *not* identify concentrations below which biological effects are never expected.

What kinds of data are used to derive AET?

An AET value is derived from paired biological and chemical data for a specific biological effect and a single chemical or group of related chemicals. Two general kinds of biological effects have been used: sediment toxicity and alterations to benthic community structure.

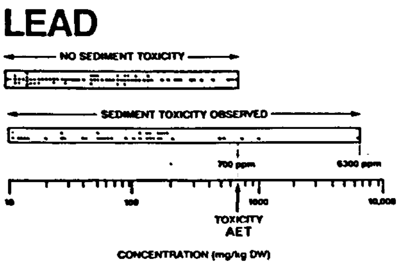
Toxicity is measured with laboratory bioassays of sensitive organisms. AET values have been established for bioassays based on three organisms: amphipods (*Rhepoxynius abronius*), larvae of the oyster *Crassostrea gigas*, and luminescent bacteria (*Photobacterium phosphoreum*). Structure of the bottom-dwelling community is examined by classifying and counting organisms found in sediments.

For both kinds of biological effects, results are compared to reference conditions to determine whether the biological effect is statistically significant.

How are AET derived?

The figure below shows the derivation of a toxicity AET for lead. Each point on the figure represents a sediment sample that was analyzed for lead (and many other chemicals) and amphipod toxicity. All available sediment samples were classified into two groups: (1) samples that did not induce statistically significant amphipod mortality relative to reference conditions (top bar) and (2) samples that did induce statistically significant amphipod mortality (bottom bar). Lead concentrations of samples within each group were then rank ordered (left to right) by increasing concentration.

The AET was established by the highest concentration at a station without statistically significant biological effects (700 mg/kg of lead in this example). Above the AET *only* significant biological effects are observed in this data set. If this AET were applied to another data set, it is expected that a high percentage of samples with lead concentrations above 700 mg/kg would be associated with amphipod toxicity.



The AET approach focuses on the fact that sediment can have concentrations as high as the AET and still have no observed effects. Thus, it is assumed in the AET approach that effects observed at concentrations below the AET for one chemical could have resulted from other chemicals present at concentrations above their respective AET value. This assumption appears to be reasonable based on validation tests of the AET approach. In these tests, a high percentage of sediment samples that were associated with biological effects (i.e., all data points in the lower bar) had one or more chemicals that exceeded their AET. A single chemical is not expected to account for toxicity in all sediments. Thus, there are samples with observed toxicity that are not accounted for by the lead AET (all samples in the lower bar to the left of the AET; see figure). However, many of these samples contain other chemicals that exceed their AET.

For which contaminants have AET been established?

AET have been developed for over 50 chemically diverse contaminants, including trace metals, polar organic compounds (e.g., 4-methyl phenol), and nonpolar organic compounds (e.g., PAH, PCBs). Selected AET are listed on the reverse side of this sheet.

How reliable are AET?

AET generated from a data set comprising 56 sediment samples were used to predict the occurrence of biological effects in sediments collected elsewhere in Puget Sound. Both sets of sediment samples had been analyzed for a wide range of chemistry and biological effects. The AET approach predicted 72-90 percent of the Puget Sound samples that had biological effects, depending on the kind of biological effects being considered.

AET can be expected to be most predictive when developed from a large database with wide ranges of chemical concentrations and a wide diversity of measured contaminants.

How have AET been used?

The AET approach has been used to identify contaminated areas of concern within Commencement Bay and Eagle Harbor. The approach has also been used to identify problem chemicals within these problem areas.

AET values (with appropriate safety factors) are being used as the basis for chemical guidelines for the disposal of dredged materials at unconfined (uncapped), open-water disposal sites for the Puget Sound Dredged Disposal Analysis program.

PUGET SOUND AET FOR SELECTED CHEMICALS (DRY WEIGHT)[a]

(ug/kg dry weight for organics; mg/kg dry weight for metals)

Chemical	Amphipod AET[b]	Oyster AET[c]	Benthic AET[d]	Microtox AET[e]
Low molecular weight PAH	5500[f,g,h]	5200	6100[h]	5200
naphthalene	2400[g,h]	2100	2100	2100
acenaphthylene	560	>560[i]	640[h]	>560[i]
acenaphthene	980[g,h]	500	500	500
fluorene	1800[g,h]	540	640[h]	540
phenanthrene	5400[g,h]	1500	3200[h]	1500
anthracene	1900[f,g,h]	960	1300[h]	960
High molecular weight PAH	38000[g,h]	17000	>51000[h,i]	12000
fluoranthene	9800[g,h]	2500	6300[h]	1700
pyrene	11,000[g,h]	3300	>7300[h,i]	2600
benz(a)anthracene	3000[g,h]	1600	4500[h]	1300
chrysene	5000[g,h]	2800	6700[h]	1400
benzofluoranthenes	3700	3600	8000[h]	3200
benzo(a)pyrene	2400	1600	6800[h]	1600
indeno(1,2,3-c,d)pyrene	880[g,h]	690	>5200[h,i]	600
dibenzo(a,h)anthracene	510[g,h]	230	1200[h]	230
benzo(g,h,i)perylene	860[g,h]	720	5400[h]	670
Total PCBs	2500[h]	1100	1100	130
Chlorinated organic compounds				
1,4-dichlorobenzene	260	120	120	110
1,2-dichlorobenzene	>350[i]	50	50	35
1,2,4-trichlorobenzene	51	64	64	31
hexachlorobenzene (HCB)	130	230	230	70
hexachlorobutadiene	290	270	270	120
Phenols				
phenol	670[g,h]	420	1200	1200
2-methylphenol	63	63	>72[i]	>72[i]
4-methylphenol	1200	670	670	670
Metals				
antimony	5.3	26	3.2	26
arsenic	93	700	85	700
cadmium	6.7	9.6	5.8	9.6
copper	800[h]	390	310	390
lead	700[h]	660	300	530
mercury	2.1[h]	0.59	0.88	0.41
nickel	>120[h,i]	39	49	28
silver	>3.7[h,i]	>0.56[i]	5.2	>0.56[i]
zinc	870[h]	1600	260	1600

FOOTNOTES

[a] AET = Apparent Effects Threshold.

[b] Based on 160 stations.

[c] Based on 56 stations (all from Commencement Bay Remedial Investigation).

[d] Based on 104 stations.

[e] Based on 50 stations (all from Commencement Bay Remedial Investigation).

[f] A higher AET (24,000 ug/kg for low molecular weight PAH and 13,000 ug/kg for anthracene) could be established based on data from an Eagle Harbor station. However, the low molecular weight PAH composition at this station is considered atypical of Puget Sound sediments because of the unusually high relative proportion of anthracene. Thus, the low molecular weight PAH and anthracene AET shown are based on the next highest station in the data set.

[g] The value shown exceeds the Puget Sound AET established in Tetra Tech (1986a) and results from the addition of Eagle Harbor Preliminary Investigation data (Tetra Tech 1986b).

[h] The value shown exceeds AET established from Commencement Bay Remedial Investigation data (Tetra Tech 1985) and results from the addition of Puget Sound data presented in Tetra Tech (1986a).

[i] ">" indicates that a definite AET could not be established because there were no "effects" stations with chemical concentrations above the highest concentration among "no effects" stations.

ANNEX 11

ACTION LIST

1. Herb Windom will review all past WGMS advice regarding the use of sediments in monitoring and will prepare an annotated list of documents produced by the WGMS on this topic.

2. Jens Skei will coordinate the first phase of the intercomparison exercise for analyses of trace metals in SPM.

3. Several WG members (Windom, Loring, Skei, Vinhas, Cato, van Geldermalsen, O'Connor) will obtain data from their laboratories regarding long-term bias and variance in replicate analyses of field samples and submit this data to the Acting Chairman by the end of March 1989.

4. The Acting Chairman will compile the information referred to in item 3 above and forward it to the Chairman of WGSATM by early April, 1989.

5. Jens Skei and Tereza Vinhas will compile information on sampling and analytical techniques used by JMP members.

6. Tom O'Connor and Leendert van Geldermalsen will each prepare a paper describing sediment-based bioassays and bioaccumulation studies in their respective countries.

7. Steve Rowlatt will prepare a paper considering further the concept of sediments as sources of contaminants.

ANNEX 12

RECOMMENDATIONS

1. The WGMS recommends that the paper "Total and partial methods of digestion for estuarine and coastal sediments and suspended particulate matter" by Loring and Rantala be published, after minor changes, in the ICES Techniques in Marine Environmental Sciences series.

2. The WGMS recommends that the WGSATM provide general guidelines on the organizing of chemical intercomparison and intercalibration exercises. The guidelines should include advice on the treatment of the data so that the overall reliability of the analytical methods used can be assessed, and so that the individual laboratory performance can be evaluated. The guidelines should also include advice on the necessary data requirements, e.g., on the number of samples of different concentrations, number of independent analyses on a sample, and other information.

3. The WGMS recommends that the WGBEC identify one of its members to attend the next meeting of WGMS to provide a briefing on the results of previous biological effects workshops (e.g., Oslo, Bermuda), to outline plans for the Bremerhaven workshop, and to discuss the possible roles of biological effects tests in future sediment-based monitoring programs.

4. The WGMS recommends that Dr. John Calder be confirmed by ICES as Chairman of WGMS.

5. The WGMS recommends that its next meeting be held for 4 days in the first half of 1990 at a time and place to be determined to conduct the following tasks:

   a) review the results of Phase 1 of the SPM intercomparison exercise and prepare plans for the continuation of the exercise;

   b) review the results of Phase 1 of the CB intercomparison exercise and prepare plans for future phases of this exercise;

   c) review past advice and guidelines prepared by WGMS regarding the role of sediments in monitoring with a view to synthesizing this information and preparing a contribution to the TIMES series;

   d) review any responses received from the WGSATM on the variance and bias data supplied by WGMS;

   e) review a paper on approaches and techniques for sediment monitoring used by various national components of the JMP;

   f) review papers on experiences with sediment-based bioassays and bioaccumulation studies in various national programs;

   g) discuss with a representative of the WGBEC the results of sediment-based bioassays applied in past biological effects workshops and the potential role of such bioassays in future operational monitoring programs; and

   h) review a paper on sediments as a source of contamination.