Advisory Committee on the Marine Environment

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

Ostend, Belgium

4–7 March 1996

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International Council for the Exploration of the Sea
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1 OPENING OF THE MEETING

The meeting of the Working Group on Marine Sediments in Relation to Pollution (WGMS) was opened at 10.00 hrs on 4 March 1996 by the Chairman, Dr S. Rowlatt. Dr K. Cooreman welcomed the participants on behalf of the Rijksstation voor Zeevisserij in Ostend, Belgium.

2 ADOPTION OF THE AGENDA

The terms of reference (C.Res.1995/2:14:2) for the meeting are listed below:

The Working Group on Marine Sediments in Relation to Pollution (Chairman: Dr S. Rowlatt, UK) will meet from 4–7 March 1996 in Ostend, Belgium, to:

a) prepare a report on the results of tests of normalisation techniques carried out intersessionally;

b) assist in the preparation of monitoring guidelines for polycyclic aromatic hydrocarbons (with MCWG and WGEAMS) with particular attention to the number of replicate samples required per sampling area to characterise the sediment sampling area and the normalisation techniques required (e.g., grain size, total organic carbon) (OSPAR 1.1);

c) review and report on an assessment of temporal trend data at various sites in the ICES area (to be carried out intersessionally by the ICES Secretariat);

d) report on the post-depositional mobility and degradation of organic contaminants in sediments;

e) review and report on standard operating procedures dealing with metal, PAH, OC pesticides and CB analyses in sediments;

f) review and report on the cycling of nutrients (especially nitrogen and phosphorus) in sediments and their release to the water column; this should be undertaken in the context of nutrient supply to phytoplankton;

g) report on the opportunities for the use of tracers (such as stable isotopes) in sediment studies, for example, in relation to the OSPARCOM monitoring objectives;

h) produce a report on variance factors in sediment metal and organic data to meet the needs of WGSAEM;

i) assess the relationship between the accumulation and the depth distribution of metals in marine sediments and the input of these same metals from local natural and anthropogenic sources to define limitations in the use of sediment metal distributions for reflecting trends in anthropogenic input functions.

The draft agenda was accepted without amendment, and is appended as Annex 1. The list of participants is attached as Annex 2. The documents attached to the report are listed in Annex 3.

3 ARRANGEMENTS FOR THE PREPARATION OF THE REPORT

Dr M. Kersten agreed to lead the discussions and to prepare the report in collaboration with Dr S. Rowlatt.

4 REPORT ON THE LATEST NORMALIZATION TECHNIQUES

A brief review of normalization methods for evaluating metal contamination of coastal marine sediments in the USA and Canada was presented by Dr D. Loring and is attached as Annex 4.

Dr S. Rowlatt presented a paper which discussed the trace metal content of sediments from estuaries around England and Wales (Annex 5). The relationship between trace metals and various normalizers (Al, Li, TOC, Md (median particle diameter)) was described.

There is a strong relationship between metals (Pb or Hg) and normalizers (Al or Li) throughout most of the Mersey estuary samples, indicating that all the sediments are from a single population (i.e., they are cogenetic). The relationship Hg vs. TOC is no better than that of Hg vs. Al. Sediments from the Manchester Ship Canal contain unexpectedly high concentrations of Pb and Hg, probably due to strong local contamination sources.

The data showed that a simple method of normalization (metal plotted vs. normalizer) could be used to rank estuary metal status by the slope of the regression and to indicate cogenetic origin of the sediment fines. This technique is particularly helpful in comparison of changes in the metal contamination status over a certain period of time. It is important to assure that the sediments are cogenetic (e.g., by measuring Pb isotope patterns of all the Mersey samples, which should be the same irrespective of the degree of contamination, cf. Section 10). Care should be taken in interpreting the results for elements which are known to be mobile under changing redox conditions.

Mr F. Smedes presented his views on the normalization of contaminants in sediments, based on the partition theory as suggested by McKay and Patterson. This theory considers that, at equilibrium, the ratio between the concentration and the uptake capacity is equal in each phase. This also applies to the different compartments within a sediment sample, i.e., it is equal for the total sample, the fraction <63 μm, the fraction <20 μm, but also for the larger fractions remaining after sieving. In normalization of sediments, the normalizing parameter is expected to represent the uptake capacity. Sieving therefore should be considered to be nothing else than providing a parallel concentration of both contaminants and normalizing parameter(s). This approach also gives a solid criterion for validation of a normalizing technique. Provided that a sample is internally in equilibrium, such a technique must give the same (not significantly different) result for different physical fractions of a single sample. This should include all sieve fractions, also a fraction obtained by sedimentation. Mr Smedes informed the Group about work he performed together with R. Varleman of the University of Berlin. In this project, one single sample from a location in the Ems-Dollard was physically separated into 14 different samples ranging from pure sand to nearly pure lutum. The range in organic carbon content was 0.1–4% and was closely related to the lutum content except for one <63 μm fraction which was obtained by ultrasonic treatment from the fraction >63 μm. Optimizing the normalization using TOC and the lutum content, it was possible to meet the above-mentioned criterion for metals, PCBs and PAHs. Taking into account the analytical error, the slopes between the contaminant content and the content of the normalizing parameter calculated for each individual sample were not significantly different from each other, even for the most sandy samples. Of course, such a validation only applies for the area investigated, and spatial comparisons cannot be made from such results.

To extend the validation for organic compounds to allow comparison between different areas, another project was initiated. Here sediments were taken from the Western Scheldt and the Wadden Sea and equilibrated with sea water by stirring. Expressed on an organic carbon basis, the contaminant concentrations in the sediments differed by a factor of four. The contaminant concentration in the water phase was sampled using semi-permeable membrame devices (SPMD, Huckins *et al.*, 1993). Since the concentration in the solid phase determines the concentration in the aqueous phase through the K_{OC} (partition coefficient related to organic carbon), the uptake rate of the SPMDs is expected to vary in proportion to the normalized concentration in the sediment. This appeared to be the case for CB153 for the two sediments studied, implying that, at equilibrium, the impact on the aqueous phase is reflected by the organic carbon normalized concentration in the sediment.

Clearly, all these approaches neeed testing on samples covering several areas before WGMS can make any firm recommendations. Normalization of the contents of organic contaminants is, however, a very important issue and more intersessional work will be done for the next meeting when this point will be taken up again.

Reference

Huckins, J. N. *et al.*, 1993. Lipid-containing semi-permeable membrane devices for monitoring organic contaminants in water. Environ. Sci. Technol. 27: 2489–2496.

5 PREPARE GUIDELINES FOR PAHs AND CBs IN SEDIMENT

WGMS agreed at its 1995 meeting to review and report on standard operating procedures (SOP) for CBs, organochlorine pesticides and PAHs. A subgroup on that topic was formed to discuss SOPs provided by a number of members of the WGMS, and to draft a technical annex to the JMP sediment guidelines on the determination of chlorobiphenyls in marine sediments. A summary of the SOPs is to be found in Annex 6. The final draft of guidelines on the determination of CBs in marine sediments (attached as Annex 7) had been extracted from a review report prepared by Smedes and de Boer on request of ICES (ICES Techniques in Marine Environmental Sciences No. 21). Although some steps of the analytical procedures reported in the SOPs differ from each other, most of these steps are in accordance with the draft guidelines. The Group discussed different technical aspects of the analysis and concluded that some procedures currently applied may possibly lead to erroneous results. This emphasizes the need for adequate guidelines.

WGMS agreed to forward the amended draft technical annex on the determination of CBs to ACME with the recommendation to approve it for inclusion in the JMP sediment guidelines.

The subgroup also took note of a document prepared by the Federal Institute of Hydrology in Koblenz (Germany). This paper discusses the analysis of PAHs in sediments and is a contribution to the development of guidelines for the latter. The Group felt that a detailed discussion of PAH analysis in relation to guidelines was not feasible in the time frame of the meeting and requires further intersessional work. The Group was also informed by two members of the MCWG, present at the meeting, that similar efforts are currently under way by that group. It was therefore suggested to coordinate the efforts of both groups. The coordinator for this subject in the MCWG (Mr R. Law) will be contacted by Dr B. Schubert for this purpose to prevent duplicate work. The organics subgroup of WGMS will take action intersessionally on those topics that are not dealt with by the MCWG.

WGMS noted that this agenda item included, in addition to discussions on analytical guidelines, the provision of advice on monitoring guidelines, including sampling strategies. The same subject had also been discussed at MCWG, and it was agreed that WGMS should start work together with MCWG to collate appropriate data. Some data on that subject are already available, and Dr I. Davies will discuss the adequacy of these data with WGSAEM in Stockholm in March 1996.

WGMS expected that this intersessional work will result in a final draft of PAH guidelines which can be evaluated by both groups during next year's meetings.

6 REPORT ON TEMPORAL TREND DATA

Dr Rowlatt presented a paper giving details of temporal trend studies off the Tyne and in Liverpool Bay. This work had been carried out as part of the UK sewage-sludge disposal site monitoring programme. Details are given in Annex 8. The data from the Tyne were produced by a stratified random sampling of sediments in an area 5 km x 5 km. The data for most metals were normally distributed and amenable to interpretation as a control chart. This approach had been used to produce a standard (average + 2s) which the sediment concentrations should not exceed. Exceedance would result in further studies being initiated to establish the cause for the increase in sediment metal concentration. This was not necessary in the period of five years considered. In contrast, the Liverpool Bay data, taken from a regular sampling grid around the area of sludge settlement, were not normally distributed. These data had therefore been interpreted as maximum, minimum and median values, and they suggested little change in the period 1979–1990.

Similar data sets have been prepared in Germany, Belgium, and the Netherlands which will be provided by WGMS members to the ICES Secretariat (Jan René Larsen) before 1 September 1996, for an assessment of temporal trend data at various sites in the ICES area. For WGSAEM to do anything qualified, the data should be accompanied by a statement of the purpose of the sampling. The Group recalled also that the 1995 meeting of the OSPAR *Ad Hoc* Working Group on Monitoring (MON 1995) had discussed whether the normalization problem could be addressed by looking at the overall variation in temporal trends. The principle of this approach is that one would apply a specific normalization technique one-by-one to data from a time series, and look for the 'best' (whatever that might be) resulting time series.

The Group felt that there is no guarantee that this will lead to a satisfactory result, but it could supplement the more geochemical discussion about normalization in sediments. This work should be progressed as a collaborative activity by sedimentologists and statisticians. The WGMS emphasized that new geochemical data from field and laboratory investigations specifically directed at the derivation of effective and reliable normalization procedures are needed. Existing data had not proved adequate to resolve the recurrent problems of normalization procedures.

Dr P. Jonsson presented some new results from the Baltic Sediment Baseline Study 1993 on retrospective assessment of temporal trends in contaminant concentrations (Annex 9). Since the 1970s there has been a substantial decrease of PCBs in biota, which has been interpreted as a decreased load due to the ban on the use of PCBs in the Baltic Sea area. The sediments, however, show a contradictory trend with increasing concentrations towards the sediment surface, indicating an increased load of PCBs to the Baltic Sea during recent decades. This is in agreement with the hypotheses of the recently launched EUCON project (Interactions between eutrophication and contaminants), that increased eutrophication may alter the distribution of chlorinated compounds in the ecosystem. Firstly, increased primary production may lead to a dilution of the contaminants in a larger biomass. Secondly, it may increase the sedimentation and subsequently lead to the scavenging of chlorinated compounds from the water mass to the sediment.

Dr F. Smedes presented some data concerning monitoring of PCBs in mussels and suspended matter at two stations in the North Sea some 10 km off the Dutch coast. The data plot shows a negative correlation between CB153 concentrations in suspended matter and the carbon content of the suspended matter, possibly as a result of dilution due to algal blooms. However, the blue mussel concentrations of CB153 were correlated to CB153 in suspended matter expressed on organic carbon content. These data indicate close relations between primary production and the distribution of contaminants in the ecosystem.

These, so far, preliminary results emphasize that contaminant trends should not be interpreted without considering changes in the eutrophication situation. The results also stress the importance of trend monitoring of contaminants not only in biota but also in sediments and suspended matter.

The Group agreed on the need for temporal trend monitoring of contaminants in Baltic Sea sediments. Laminated sediments reported from several areas in the Baltic Sea may offer particularly promising conditions for future trend monitoring

7 REPORT ON POST-DEPOSITIONAL MOBILITY OF ORGANIC CONTAMINANTS

Dr Jonsson presented some results from the Baltic Sea concerning degradability of extractable organic chlorine (EOCl) compounds (Annex 10). The results from an EOCl mass balance study suggest that a major part of the total input of EOCl since the 1940s is still stored in the Baltic sediments, indicating a significant persistence for EOCl. These results were supported by a two-year incubation study of pulp mill contaminated sediments, which indicated a degradation half-time for EOCl of decades rather than months or years. Also, treatment of the EOCl extracts with concentrated sulphuric acid showed that a substantial part (10–15 %) of EOCl is resistant to oxidation.

Dr Kersten presented a report on PAH efflux rates from sediment cores sampled in the Chesapeake Bay and incubated in the laboratory (Helmstetter and Alden, 1994). The observed flux rate coefficient k (= efflux rate over sediment concentration) correlates well with the solubility and K_{OW} coefficient of PAHs. It appears possible to predict flux rates of other hydrophobic organic chemicals from ambient sediment and water concentrations, K_{OW} information, and the empirical model proposed by the authors, indicating that efflux is negligible with respect to the inventory in the sediment.

In the discussion, Dr Naes referred to his results on PAH hot spot surveys. Numerical reanalysis of a large number of surface and downcore samples from seven Norwegian fjords affected by smelter-generated PAHs strongly indicate that these compounds are not available to post-depositional transformation reactions.

The Group came to the conclusion that post-depositional geochemical mobility (in contrast to physical mobility such as hydro- and bioturbation) does not seem to have any relevance to PAHs nor probably to other hydrophobic contaminants monitored in sediments, but may have considerable effect on concentrations in the overlying water phase. It is also important to recognize that petrogenic PAHs may differ from pyrogenic PAHs but the reviewed information relates only to the latter.

References

Helmstetter, M.F., and Alden III, R.W. 1994. Release rates of PAHs from natural sediments and their relationship to solubility and octanol-water partitioning. Arch. Environ. Contam. Toxicol., 26: 282–291.

Naes, K., *et al.*, 1995. Mobilization of PAH from polluted seabed and uptake in the blue mussel. Mar. Freshwater Res., 46: 275–285.

Naes, K., and Oug, C. 1996. PAH in sediments from Norwegian smelter-affected fjord and coastal waters: I. A multivariate approach to transport and incorporation, and II. A multivariate approach to the postdepositional fate of PAHs. (Both papers submitted to Environ. Sci. Technol).

8 REPORT ON SOPS FOR METAL, PAH, OC PESTICIDE, AND CB ANALYSES

Three SOP packages on trace metals submitted intersessionally to WGMS will be distributed among interested members. The Group felt that there is no need to discuss the SOPs in great detail because the most suitable techniques are already mentioned in the JMP sediment guidelines and other available technical reports (e.g., Loring, 1992).

Organic contaminants were considered in a subgroup formed to discuss SOPs provided by a number of members of WGMS. A summary of the SOPs is contained in Annex 6. Although some steps of the analytical procedures reported in the SOPs differ from each other, most of these steps are in accordance with the best available techniques listed in a report prepared by Smedes and de Boer (ICES Techniques in Marine Environmental Sciences No. 21). The Group discussed different technical aspects of the analysis and concluded that some procedures currently applied may possibly lead to erroneous results. This emphasizes the need for adequate guidelines (cf. Section 5).

9 REVIEW AND REPORT ON CYCLING OF NUTRIENTS

The WGMS was asked to consider the behaviour of nutrients in marine sediments, taking particular note of the issues raised in the North Sea Quality Status Report (QSR) (Oslo and Paris Commissions, 1993). However, it turned out that not much information on this topic is contained in the QSR, and that most literature on nutrient cycling is devoted to lacustrine and estuarine environments. The Group was informed by members from Denmark and Sweden, however, that there are major surveys on this topic under way in both countries. The results of these studies will be made available for the next meeting, where this topic will be discussed in more detail.

The WGMS recommended that it discuss biogeochemical processes in the uppermost seafloor in relation to organic matter and nutrient cycling at its next meeting. This discussion should rely on intersessional reports prepared on this topic and on an expert invited to present the most recent results of scientific research.

10 REPORT ON THE USE OF TRACERS IN SEDIMENT STUDIES

The use of stable lead isotope patterns represents a powerful alternative to current normalization techniques to distinguish between natural and anthropogenic Pb in marine sediments. Because three of the four stable Pb isotopes are produced by the radioactive decay of their uranium and thorium parent nuclides, stable Pb isotope ratios (e.g., $^{206}Pb/^{207}Pb$) depend on the age and primeval characteristics of the geological system from which the Pb derives, i.e., the source of the lead. As a result, the isotopic signature of anthropogenic Pb in marine sediments is usually different from that of background Pb. Dr M. Kersten presented examples showing that ICP/MS is a useful analytical technique to discriminate between the different Pb sources not only in sediments but also in other compartments of the marine ecosystem on the basis of isotope pattern analysis (Krause *et al.*, 1993). It is particularly suitable not only to assess the pathway to and proportion of gasoline-derived Pb in sediments, but also the uptake route of Pb to benthic organisms (Kersten *et al.*, 1992).

Considering that many laboratories will most likely have access to an ICP/MS instrument in the near future, the Group recognized that Pb isotope ratios will soon be of great utility in both spatial and temporal monitoring programmes (including retrospective assessments using sediment cores) for contaminants in sediments. It was emphasized, however, that this technique works for Pb but not for other trace metals.

References

Kersten, M. *et al.*, 1992. Pollution source reconnaissance using stable lead isotope ratios. pp. 311–325. In Impact of Heavy Metals on the Environment. Ed. by J.-P. Vernet. Elsevier, Amsterdam.

Krause, P. *et al.*, 1993. Determination of isotope ratios by ICP-MS in particulate matter from the North Sea environment. Fresenius J. Anal. Chem., 347: 324–329.

11 REPORT ON VARIANCE FACTORS IN SEDIMENT METAL AND ORGANIC DATA

Dr Smedes reported on the sampling variability for organic contaminants in coastal sediments off the Netherlands. The outline of and data from his report are included in Annex 11. He concluded that sampling variability due to physical inhomogeneity in the sampling area can be reduced by normalization (e.g., grain size fractionation).

Dr Davies also presented some data on variability from QUASIMEME (Annex 12).

12 REPORT ON THE RELATIONSHIP BETWEEN INPUTS AND METAL DISTRIBUTIONS IN SEDIMENTS

Dr P. Jonsson presented a paper concerning large-scale metal distributions in the Baltic Sea during a meeting of a metal subgroup formed to discuss that topic. The data have been used in two mass balance studies (Borg and Jonsson, 1996).

For the Gulf of Bothnia and the Åland Sea, the annual loads of trace elements have been estimated for the 1980s. Sediment data, valid for the same period, indicate that only about half the loads of cadmium, copper, zinc and mercury are sequestered in the sediments of the Gulf of Bothnia. The rest is most likely exported to the Baltic Proper. These conclusions are supported by high sediment concentrations, especially of cadmium, in the northern part of the Baltic Proper.

Regarding the entire Baltic Sea, the total annual cadmium input during the 1980s has been estimated to average 140 tonnes/year. The estimation of the annual sequestering of Cd in Baltic Sea sediment (113 tonnes) is in good agreement with the estimates from measurements of Cd in water, leading to an estimated retention time in the water mass of about five years. The major part of the cadmium input is sequestered in the laminated sediments of the Baltic Proper, especially in the northern half, where the mean sediment cadmium concentrations are more than five times the concentrations in the southern half.

Recent cadmium profiles from the Baltic Sea Sediment Baseline Study indicate substantially decreasing sediment concentrations during the last 5–10 years. In time, this seems to correspond to significant increases in pelagic biota in the Baltic Sea.

The Group discussed the extent to which the Cd export to the Baltic Proper might be controlled by post-depositional mobilization due to early diagenetic processes. The strong enrichment of Cd in the uppermost sediment layers of the Gotland Deep can be interpreted as an excess deposition of metal sulphides from the anoxic (sulphidic) overlying water to the anoxic sediments. This points to a large-scale metal redistribution by a process of post-depositional mobilization from oxygenated sediments of the Gulf of Bothnia and the Åland Sea and a precipitation of Cd imported from those areas in the sulphidic Gotland Deep waters. The assumption of a widespread post-depositional redistribution of trace metals in Baltic Sea sediments needs further investigations, in particular concerning the time scales on which such post-depositional redistribution may occur.

The metal subgroup accepted that the process of trace metal redistribution along redox gradients has to be considered for sediment monitoring in the entire Baltic Sea and emphasized that similar work should be undertaken in regions of the OSPAR area. Intersessional work will be coordinated by Dr Kersten in order to survey the available data.

Dr C. Janssen from Ghent University was invited to give a talk on the use of toxicity identification procedures for the characterization of dredged sediment. The toxicity of sediment pore waters from four sites in the Upper Scheldt was characterized using modified Toxicity Identification Evaluation (TIE) procedures. The samples from all locations exhibited acute toxicity to the freshwater crustacean *Thamnocephalus platyurus*. The TIE approach was conducted using an enlarged battery of contaminant speciation fractionation tests. Toxicity was removed or at least significantly reduced by purification of the pore water by cation exchange resins or by air-stripping at pH 11. Increased toxicity was observed at higher pH values, while a reduced toxicity was found after decreasing the pH. From this TIE pattern, ammonia was identified as the dominant toxic agent which was found at 150 mg/l levels in the pore water.

Reference

Borg, H., and Jonsson, P. 1996. Large-scale metal distribution in Baltic Sea sediments. Mar. Pollut. Bull., 32: 8–21.

13 ANY OTHER BUSINESS

13.1 Re-drafting of sediment guidelines

The WGMS has initiated discussion on new sediment guideline annexes for organic contaminants (PAHs and CBs) which may necessitate a revision of part of the main text of the guidelines. Due to some uncertainty over whether the sediment guidelines were on the agenda or not, the organic subgroup was not equally prepared to discuss this in detail.

Since the existing guidelines do not contain substantial information on organic contaminants, the Group considered that the present state of knowledge allows an expansion with respect to this group of contaminants. Within the time frame of this meeting it was not feasible to achieve this. However, it was recognized that, for example, the following items should be dealt with:

- terms such as 'degree of contamination' and 'sediment quality' should be specified for organic contaminants;
- whether the sampling strategy differs from that for heavy metals should be considered;
- normalization of the organic contaminants should be reviewed;
- possible degradation or transport of organic compounds should be taken into account for retrospective trend assesment;
- advice on treatment of sediments should be updated with respect to organic compounds.

Guidance on analytical methods has been prepared for CBs (see Annex 7) and is in progress for PAHs.

In the discussion, it turned out that reaching agreement on normalization is vital in relation to some of the items outlined above. In preparation for the next meeting, B. Schubert and F. Smedes agreed to work intersessionally to investigate the possibility of developing a normalization approach which does not require major changes in the methods currently applied.

13.2 Future of the JMSBEC

In response to the decision made in the previous week by the JMSBEC, the future possible role of the JMSBEC was discussed jointly by WGMS and WGBEC. It was agreed that the JMSBEC had largely achieved its initial aim to develop conceptual frameworks for the integration of chemical measurements in sediments and biological effects measurements. The more specific recommendations of the JMSBEC for ways in which to integrate chemistry and biology (at various levels of organization) have been well received by ACME, and the principles have been adopted by OSPAR for application within its new Joint Assessment and Monitoring Programme (JAMP).

It was generally agreed that the JMSBEC was trying to address fundamental questions relating to the significance of contaminants in sediments, and the bioavailability of these contaminants. These were the underlying justification for including sediment chemistry in quality assessment programmes. The need to be able to assess whether a particular concentration of a contaminant presented a hazard to organisms is as vital as ever. However, the meeting agreed that there had been few new developments in this area since the 1995 JMSBEC, and this had been reflected in the 1996 JMSBEC report.

The meeting discussed new areas in which the JMSBEC might be able to foster new cooperation between biological effects workers and sedimentologists. Several suggestions were made, including greater emphasis on the processes within sediments leading to solubilization and release of contaminants from sediments. The biogeochemistry of contaminants in sediments linked sediment geochemistry with the role of bacteria in sediments. Mobilization was also connected to physical and biological mixing processes such as the role of bioturbation, etc. It was felt that the links between solid phase sediment chemistry and water phase (overlying and pore water) required strengthening. It was suggested that the exchange of nutrients between sediment and water might warrant the invitation of a nutrient geochemist to a JMSBEC meeting, and that the inclusion of an organic physical chemist with environmental interests might also give rise to the recognition of new perspectives and activities.

There is continuing pressure to develop Sediment Quality Criteria—a process that inevitably requires the combination of chemical and biological data. There has been considerable interest in this area in North America, and regulatory authorities in Europe periodically indicate that reliable criteria would be useful to them.

It was concluded from the joint session that the two Working Groups should consider the development of new directions for investigating the links between sediment chemistry and biological processes intersessionally, and would include items in this area in their proposed terms of reference for 1997. In recognition that the process leading to well-considered new proposals for activities by the JMSBEC would need some time to yield substantive output, it was agreed to recommend that the JMSBEC should not meet in 1997, but that opportunity for joint sessions of WGMS and WGBEC should be created within the framework of the 1997 meetings by requesting that the two Working Groups meet at ICES Headquarters during the same week, with a view to planning a JMSBEC meeting in 1998.

13.3 Paper Presented by Local Sedimentologists

Dr P. Roose presented a paper by Vyncke and Hillewaert on 'Colour measurements on marine sediments off the Belgian coast as a means for estimating grain size'.

13.4 Chairmanship of WGMS

Although Dr S. Rowlatt had resigned from the Chairmanship at the 1995 WGMS meeting, for administrative reasons he had been asked to chair the 1996 meeting.

Dr Rowlatt confirmed his resignation, and the Group unanimously confirmed their nomination of Dr M. Kersten to be the new chairman of WGMS.

14 RECOMMENDATIONS AND ACTION LIST

In terms of the next meeting of the Working Group, the WGMS recommended that it meet for four days in March 1997 in Copenhagen, Denmark, concurrently with the WGBEC meeting. Nine tasks were proposed for the terms of reference. The full list of recommendations is contained in Annex 13.

The WGMS agreed to recommend that ACME adopt the Annex on CB analysis in sediments as a new Technical Annex to the ICES sediment guidelines.

The WGMS agreed furthermore to recommend that ICES ask the Danish Delegate to invite to the next meeting of the Working Group an expert to report on the most recent results of research in nutrient cycling between sediments and water, e.g., Dr Lomstein from Aarhus University.

The following intersessional activities were agreed to be undertaken:

1. Drs Rowlatt, Roose, Jonssen and Kersten to send Jan René Larsen (ICES Secretariat) data and assessment of data on time series monitoring of contaminants in sediments by 1 September 1996. Jan René Larsen to compile and summarize this information.

2. All members to assist Dr Kersten in the production of a report on biogeochemical processes in sediments in relation to trace metal speciation and mobility.

3. All members to assist Dr Smedes in the production of a review on methods to investigate particle-water interaction of organic contaminants in the marine environment.

4. Dr Jonsson to prepare a report on the results of Swedish surveys on nutrient cycling between sediment and water in the Baltic Sea, in particular with respect to the denitrification potential and secondary pollution potential for phosphate.

5. Dr Davies to report on the fate of fish farm medicines in sediments.

6. Dr Naes to report new data on toxicological effects of PAHs in sediments, in particular with regard to changes in benthic community structure.

7. Dr Schubert to contact Mr Law from MCWG to coordinate the intersessional work on the PAH guidelines.

8. Dr Smedes to report data which may help in establishing appropriate normalizers for organic contaminants.

9. Dr Davies to discuss the adequacy of available data for evaluating the sampling strategy for organic contaminant monitoring in sediments in collaboration with WGSAEM.

15 ADOPTION OF THE REPORT

The meeting considered and approved the report of the WGMS.

16 CLOSING OF THE MEETING

The meeting was closed by the Chairman at 15.00 hrs on 7 March 1996.

ACRONYMS (not defined in report)

JMP	Joint Monitoring Programme of the Oslo and Paris Commissions
MCWG	ICES Marine Chemistry Working Group
WGEAMS	ICES Working Group on Environmental Assessment and Monitoring Strategies
WGSAEM	ICES Working Group on Statistical Aspects of Environmental Monitoring
WGBEC	ICES Working Group on Biological Effects of Contaminants
JMSBEC	Joint Meeting of the Working Group on Marine Sediments in Relation to Pollution and the Working Group on Biological Effects of Contaminants

ANNEX 1

AGENDA

Working Group on Marine Sediments in Relation to Pollution
Ostend, Belgium

4–7 March 1996

1) Opening of the meeting
2) Adoption of the agenda
3) Arrangements for the preparation of the report
4) Report on the latest normalization techniques
5) Prepare guidelines for PAHs in sediments
6) Report on temporal trend data
7) Report on post-depositional mobility of organic contaminants
8) Report on SOPs for metal, PAH, OC pesticide, and CB analyses
9) Review and report on cycling of nutrients (particularly nitrogen and phosphorus)
10) Report on the use of tracers (such as stable isotopes) in sediment studies
11) Report on variance factors in sediment metal and organic data to meet the needs of WGSAEM
12) Report on the relationship between inputs and metal distributions in sediments
13) Assess proposals for the re-drafting of sediment guidelines
14) Any other business
15) Recommendations and action list
16) Closing of the meeting

ANNEX 2

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ANNEX 3

LIST OF MEETING PAPERS

WGMS 1996/1	Krause, P., Kriews, M., Dannecker, W., Garbe-Schönberg, C.D., and Kersten, M. 1993. Determination of $^{206/207}$Pb isotope ratios by ICP-MS in particulate matter from the North Sea environment. Fresenius J. Anal. Chem., 347: 324–329.
WGMS 1996/2	Jonsson, P. and Granmo A. Degradability of extractable organic chlorine (EOCl).
WGMS 1996/3	Jonsson, P. Some data on offshore temporal trends in the Baltic Sea.
WGMS 1996/4	Rowlatt, S., Limpenny, D., Hull, S., Jones, B., Whalley, C., Salmons, M., Jones, L., Lovell, D. and Deacon, C. Extract from an assessment of metals in estuarine sediment.
WGMS 1996/5	Rowlatt, S. An extract from the final report of the Metals Task Team of the Group Coordinating Sea Disposal Monitoring (GCSDM).
WGMS 1996/6	Guideline for the determination of polycyclic aromatic hydrocarbons (PAH) in sediments—analytical method.
WGMS 1996/7	Helmstetter, M.F. and Alden, R.W. 1994. Release rates of polynuclear aromatic hydrocarbons from natural sediments and their relationship to solubility and octanol-water partitioning. Arch. Environ. Contam. Toxicol., 26: 282–291.
WGMS 1996/8	Kersten, M., Förstner, U., Krause, P., Kriews, M., Dannecker, W., Garbe-Schönberg, C.D., Hock, M., Terzenbach, U. and Grassl, H. Pollution source reconnaissance using stable lead isotope ratios ($^{206/207}$Pb).
WGMS 1996/9	Jonsson, P. and Borg, H. 1996. Large-scale metal distribution in Baltic Sea sediments. Marine Pollution Bulletin, 32: 8–21.
WGMS 1996/10	Vyncke, W. and Hillewaert, G. Colour measurements on marine sediments off the Belgian coast as a means for estimating grain size.
WGMS 1996/11	Guidelines for the use of sediments in marine monitoring in the context of Oslo and Paris Commissions programmes.

ANNEX 4

NORMALIZATION MODELS FOR EVALUATING METAL CONTAMINATION OF COASTAL MARINE SEDIMENTS

Problem

Coastal sediments receive metal contamination from land-based activities along with natural metal inputs due to natural watershed weathering and erosion processes. Metal levels in coastal sediments, arising from natural processes, are not generally amenable to management, nor should they be, because metals occurring naturally in sediment are of little concern *vis-à-vis* biological effects (i.e., they are predominantly bound in mineral lattices and thus not readily available to organisms).

Anthropogenic metal levels in coastal sediments are more likely to exert biological effects. Therefore, it is important to establish strategies to manage these metal inputs. Typically, these strategies are based on programmes that monitor the spatial and temporal variability of metal concentrations in sediments. The problem, however, is that natural and contaminant metal levels are often confused. This confusion may lead to the adoption of management strategies based on natural metal variations and this can result in misplaced perceptions of problems (i.e., that metal concentration gradients imply the presence of anthropogenic sources where none exist).

Objective

To discriminate between anthropogenic and natural contributions to metals in sediments. Such a model is needed to allow such discrimination to be achieved on the basis of data that are readily obtainable by contemporary techniques for sediment contaminant monitoring.

Model and Data Requirements

Natural metals are contained in a relatively few naturally occurring aluminosilicate-type minerals, such as phyllosilicates (i.e., clay minerals). Because of their relatively fragile, soft nature they tend to be more concentrated in the fine grain-size fraction of sediments. Thus, variations in the grain-size distribution of sediments exert a major control over natural metal concentrations in sediments. These variations can be compensated for by normalizing metal concentrations in sediments to mean grain size or by selecting a specific grain-size fraction to account for natural variations, so that superimposed, anthropogenic augmentations can be distinguished. It is far more practical, however, to use geochemical normalizers, such as aluminium, to account for the natural metal-bearing phases. Such methods have been described by Windom *et al.* (1989) and Loring (1990) using Al and Li, respectively, as geochemical normalizers for different sedimentary environments in which natural metal concentrations are found to be linearly correlated to the normalizer concentration.

To establish a model for evaluating metal contamination, a population of sediment samples, reasoned to be essentially contaminant free, are collected for a region and analysed for the metals of interest and the selected geochemical normalizer. Statistical analysis, using the approach of Schropp *et al.* (1990), is then applied to the data resulting in the development of a model that predicts expected naturally derived metal concentrations, within a 95% confidence limit, in natural sediments in relation to the concentration of the geochemical normalizer. The difference between the observed and the predicted concentrations of a metal of interest provides a direct measure of the degree of contamination.

Application

Ten to fifteen years ago, the observed variations in metal concentrations of sediments from the northern and southern Florida coasts were assumed to be due to contamination when. in fact, they were natural. Using the normalization model, areas of naturally low metal concentration could be identified as contaminated even though they contained considerably lower sedimentary metal levels than some other uncontaminated areas (Windom *et al.*, 1989). Before the model was applied, management strategies were focused on areas containing higher, but entirely natural sediment metal concentrations.

References

Loring, D.H., 1990. Lithium - a new approach for the granulometric normalization of trace metal data. Marine Chemistry, 29: 155–168.

Schropp, S.J., F.G. Lewis, H.L. Windom, J.D. Ryan, F.D. Calder and L.C. Burney, 1990. Interpretation of metal concentrations in estuarine sediments of Florida using aluminum as a reference element. Estuaries, 13 (3): 227–235.

Windom, H.L., S.J. Schropp, F.D. Calder, J.D. Ryan, R.G. Smith, Jr., L.C. Burney, F.G. Lewis and C.H. Rawlinson, 1989. Natural trace metal concentrations in estuarine and coastal marine sediments of the southeastern United States. Environmental Science and Technology, 23: 314–320.

ANNEX 5

GEOCHEMISTRY OF SOME ESTUARINE SEDIMENTS

The data from this project are discussed in the following sections. However, in order to illustrate the general principles employed, Mersey estuary sediments are discussed first as they provide a good example of the effective use of normalization.

The application of normalization to sediments from the Mersey

The mean metal contents of the sediments from the estuary are shown in Table A5.1. The metal concentrations decrease in the order, docks > lock entrances > sea channels > Eastham Channel. This correlates with the sediment types in these areas which range from mud in the docks to sand in Eastham Channel.

In the relatively quiescent environment of the docks, particulates settle from the water column and have to be dredged periodically in order to maintain access to berths. In other, more hydrodynamically active areas of the Mersey system (e.g., the sea channels and Eastham Channel) both lateral bedload transport and sedimentation are important factors in the siltation of navigational channels. These differences in hydrodynamic regime are reflected in the sediments deposited in the various areas: mud in the docks; sandy mud in the lock entrances; muddy sand in the approach channels to the Mersey; and sand in the Eastham Channel. Overall, the sands contain concentrations of trace metals lower than those of the muds because quartz particles generally contain only very low concentrations of trace metals.

Quartz in mud/sand mixtures acts as a diluent, lowering sediment metal burdens. In order to eliminate this diluent-induced variability, it is possible to examine the relationship between the metal and a conservative element associated with the contaminant-bearing fraction of the sediment. In this case, conservative refers to a non-contaminant element of only limited reactivity in the environment of interest—and aluminium is the element of choice.

The dock dredgings are contaminated with, amongst other metals, mercury derived from industry in the Mersey catchment area and they contain a range of mercury concentrations from 0.4 to 3 mg/kg. Sediments from the Mersey Estuary have mercury contents ranging from 0.02 to 2.5 mg/kg. However, direct comparison of the dock dredgings with the estuarine sediments is made difficult by the fact that the latter sediments contain a large amount of quartz relative to those in the docks.

The position can be clarified by use of the conservative element normalization technique, as follows. Figure A5.1 shows a strong correlation between the mercury and aluminium contents of the sediments from the Mersey Estuary and its associated docks. As aluminium is primarily located in the structure of the clay minerals, it is effectively a marker for them. These data, therefore, indicate that mercury is strongly associated with the clay minerals, either directly or by adsorption onto organic coatings.

Some mercury will be present in the lattice structure of the clay minerals. However, as the mercury content of average shale is 0.4 mg/kg (Krauskopf, 1967) compared with about 4 mg/kg in the muddiest samples from Liverpool docks, it is unlikely that mercury in clay mineral lattices contributes significantly to the total mercury burden of the sediments.

The relationship shown in Figure A5.2 indicates that the sediments all contain the same level of contamination in the metal-bearing clay fraction and that the sediments are mixtures of two particle populations, a mercury- and aluminium-bearing population (the clays) and a low-mercury population (the sands). Similar relationships were observed by Rowlatt (1988) using iron as a normalizer.

These sediments, taken throughout the Mersey Estuary and the dock areas of Liverpool, are part of a continuum from sand to mud. Thus, the normalization technique has identified the fine sediments throughout the sample domain as constituting one population.

Any exceptionally contaminated material (i.e., not from the same fines population) would have shown up as outliers to the main trend line. This effect is illustrated in Figure A5.2 where samples from the Manchester Ship Canal (MSC) can be seen to deviate markedly from the mercury/aluminium relationship.

In conclusion, the concentration of contaminants in sediments collected from the Mersey/Liverpool docks system depends largely on the fines content of the sediments and normalization against aluminium suggests that there is only one population of fines in the area.

The use of sediment metal data to assess the quality of the Mersey estuary

Table A5.1 shows the concentrations of metals in sediments in the Mersey Estuary and shows, for example, that cadmium concentrations range between 11 and 2000 µg/kg and mercury concentrations range between 8.8 and 4000 µg/kg. Any classification system that uses raw concentrations will therefore be subject to enormous variability depending on where the samples are collected: in a high metal area (muddy) or in a low metal (sandy) area.

The previous discussion of the Mersey data showed that all the sediment samples taken in the Mersey estuary area are part of the same general population, with the exception of those from the Manchester Ship Canal (MSC). Thus, a parameter which describes the whole population filtered to remove outliers will be insensitive to variations in sampling location and can be used to describe sediments in the whole estuary. A measure which should be considered as a candidate for this role might be the slope of the relationship between metal and normalizer.

The previous discussion used aluminium as a normalizer, however, the present dataset also includes lithium, organic carbon and particle size as potential normalizers. Figures A5.3 to A5.6 show these normalizers plotted for lead against aluminium.

Lithium appears to be as effective as aluminium (Figures A5.3 and A5.4), but the others are less so. The particle size normalizer (median diameter in the <500 µm size fraction) shows a degree of correlation in the finer sediments which is less marked the coarser the sediment. Organic carbon may be more suited to particular elements, and in this respect mercury is often cited as an organic-associated element. Figure A5.7 shows mercury plotted against organic carbon and indicates a reasonably strong relationship, although not markedly stronger than against aluminium (Figure A5.1).

Of course, the above argument applies to the Mersey Estuary and may or may not be applicable elsewhere. In particular, this estuary may be ideal for normalization because the Mersey Estuary is very well mixed, due largely to its macrotidal nature.

Table A5.1 General statistics of samples collected from the Mersey estuary.

Variable	N	Mean	Std. Dev.	Minimum	Maximum
Al (%)	45	3.35	1.83	0.93	6.36
Cd (µg/kg)	45	639.46	528.38	11	2555
Cr (mg/kg)	45	70.68	47.08	<11	152
Cu (mg/kg)	45	37.68	33.23	1.36	107.2
Fe (%)	45	2.04	1.11	0.51	3.86
Hg (µg/kg)	44	1823.39	3655.67	8.8	19609
Li (mg/kg)	45	32.03	20.75	0.9486	70.21
Ni (mg/kg)	45	22.17	15.32	<3	48.3
Pb (mg/kg)	45	104.35	147.98	2.176	812.3
Zn (mg/kg)	45	211.34	152.54	2.659	651.1
As (mg/kg)	45	16.02	8.41	<0.2	38.54
V (mg/kg)	45	49.97	32.31	1.61	107
OC (%)	45	1.19	0.98	0.03	3.78
MED (µm)	22	139.29	106.25	16.34	360.6

Application of candidate measure of sediment quality to various estuaries

It was suggested in the previous section that the slope of the regression between metal and normalizer in sediments might be an indicator of the general sediment metal status of the Mersey. This section considers whether this method would have wide application.

Figure A.5.8 shows the relationship between lead and aluminium in various estuaries. Regression lines are drawn through the datasets for most estuaries especially those where a strong relationship is apparent, and Table A5.2 lists the relationships and R-square values for the relationships ranked by the size of slope.

The relationships shown here have been calculated with the relatively small numbers of samples produced in this project and may change when more comprehensive datasets become available. In particular, it should be noted that the regression can only be taken to represent the areas sampled. Further sampling should be carried out to test the method more widely. The datasets used in Figure A5.9 have been filtered to remove particularly high values which may represent contamination (e.g., those from the Manchester Ship Canal). Despite these limitations, this work demonstrates the potential general applicability of the method.

The R-squares shown in Table A5.2 are generally high, indicating good correlation between lead and the normalizer. The values are ranked by size of slope, the higher values indicating the estuaries or parts of estuaries with higher sediment metal status. It must be borne in mind that a high sediment metal status only indicates relatively high metal concentrations, not whether the metal is of natural or anthropogenic origin. In order to assess the origin of the metal, samples from cores or from known uncontaminated areas would need to be collected, preferably with dating of the cores, to assess background concentrations. The present data are amenable to further analysis to clarify this methodology, although the tight time restrictions on this project have prevented this.

Figure A5.9 shows the relationships between mercury and aluminium and suggests that the proposed method is valid for mercury as well as lead.

Table A5.2 Relationships between lead and aluminium in various estuaries.

Estuary	Regression relationship	R-square
Medway	y=34.94-89.40	0.88
Tamar	y=33.79x-52.94	0.64
Mersey	y=27.96x-17.92	0.72
Derwent	y=18.35x-22.07	1.0
Wye	y=16.48x-18.19	0.63
Wye	y=16.48-18.19	0.63
Severn	y=15.39x-7.84	0.74
Solway Firth	y=15.03x-20.59	0.63
Bristol Avon	y=14.95-1.94	0.70
Usk	y=14.75x-5.19	0.39
Avon	y=13.72x+6.90	0.22
Dart	y=12.092x-8.52	0.89
Cleddau	y=11.03x-4.83	0.73
Humber	y=7.52+11.66	0.53
Taw	y=6.75x+5.55	0.87
Adur	y=3.97x+7.02	0.54
Conwy	y=3.92x+8.10	0.33

Figure A5.1 The relationship between mercury and aluminium in sediments from the Mersey estuary.

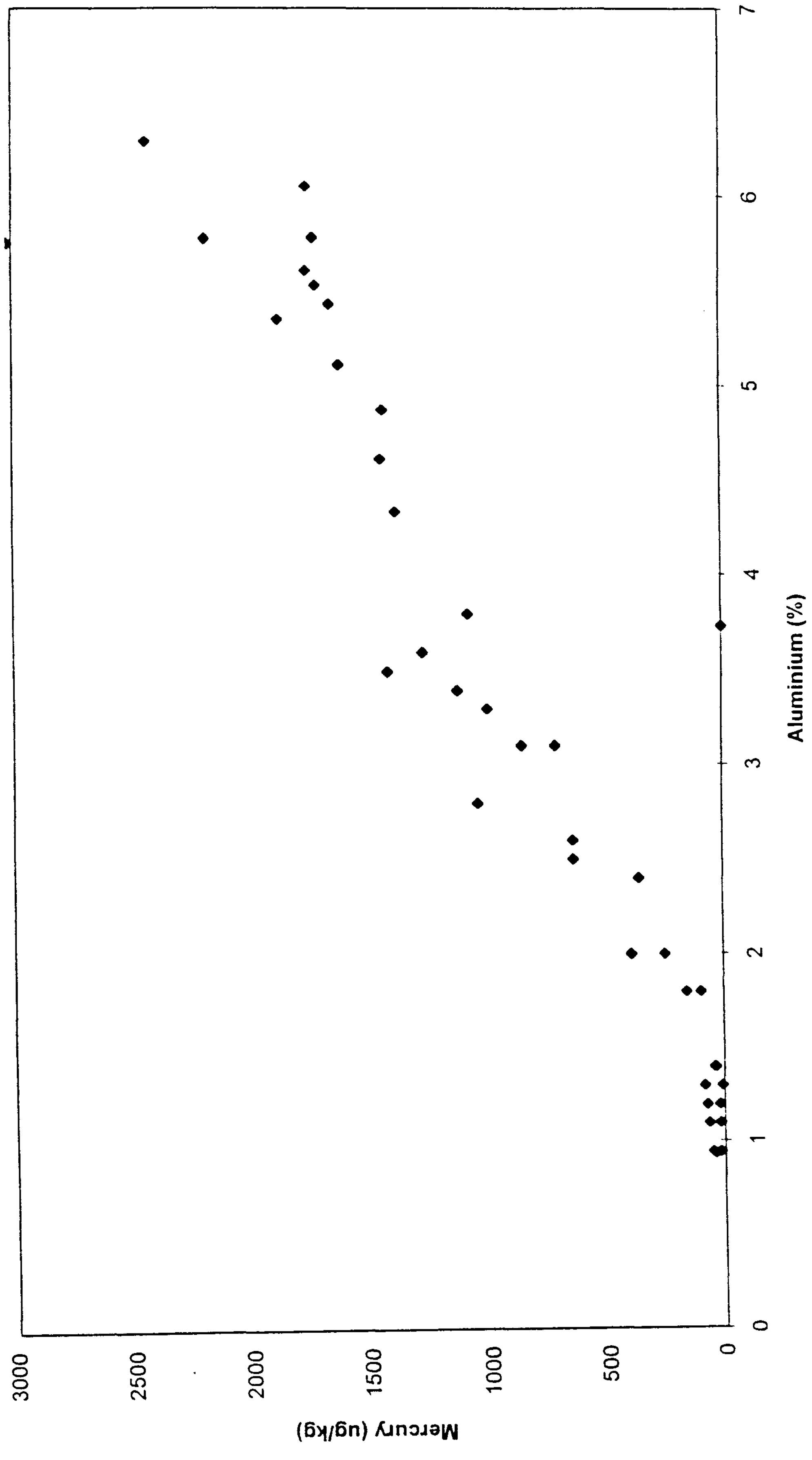


Figure A5.2 The relationship between mercury and aluminium in sediments from the Mersey estuary and Manchester Ship Canal (MSC).

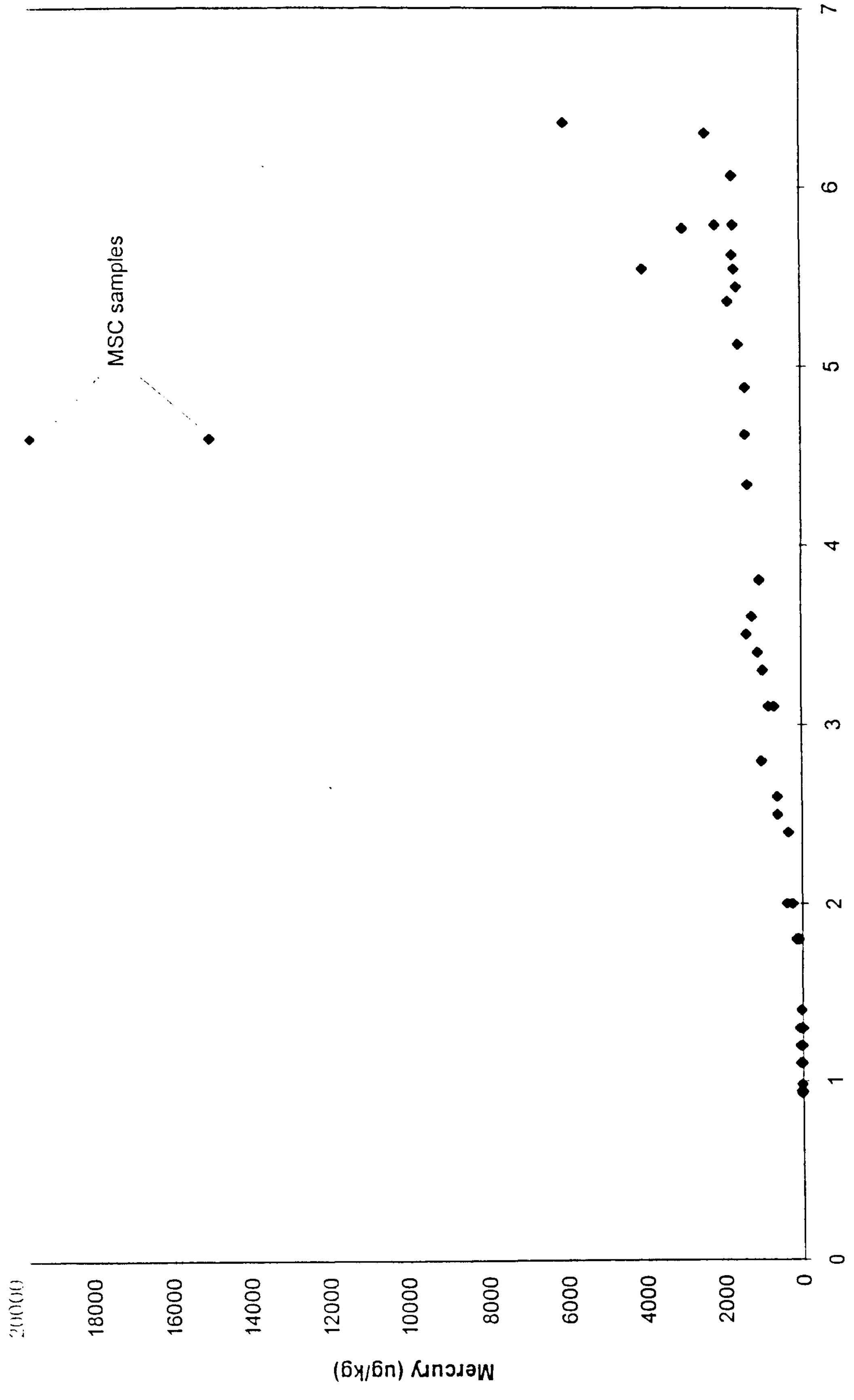


Figure A5.3 The relationship between lead and aluminium in sediments from the Mersey estuary.

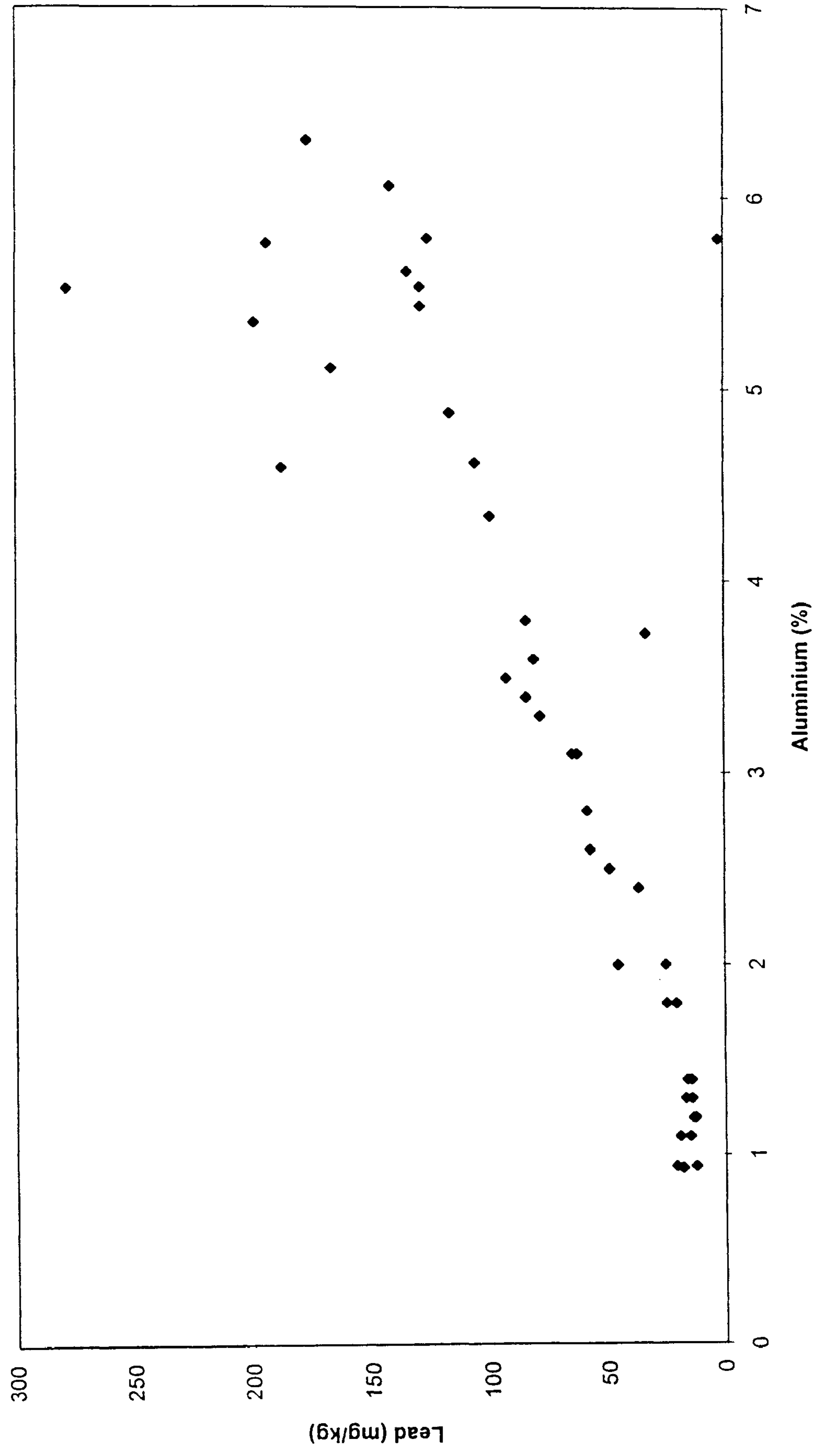


Figure A5.4 The relationship between lead and lithium in sediments from the Mersey estuary.

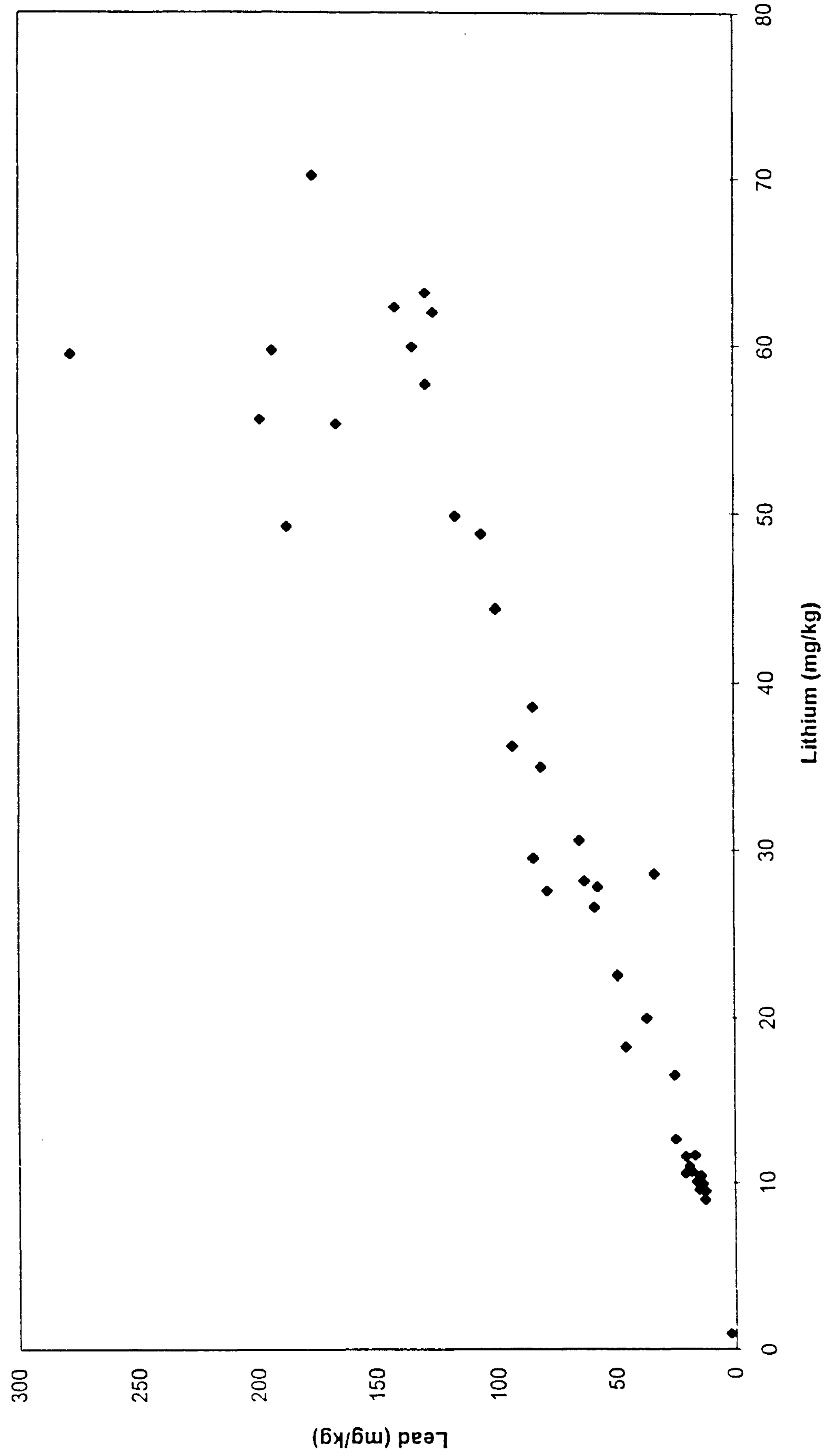


Figure A5.5 The relationship between lead and organic carbon in sediments from the Mersey estuary.

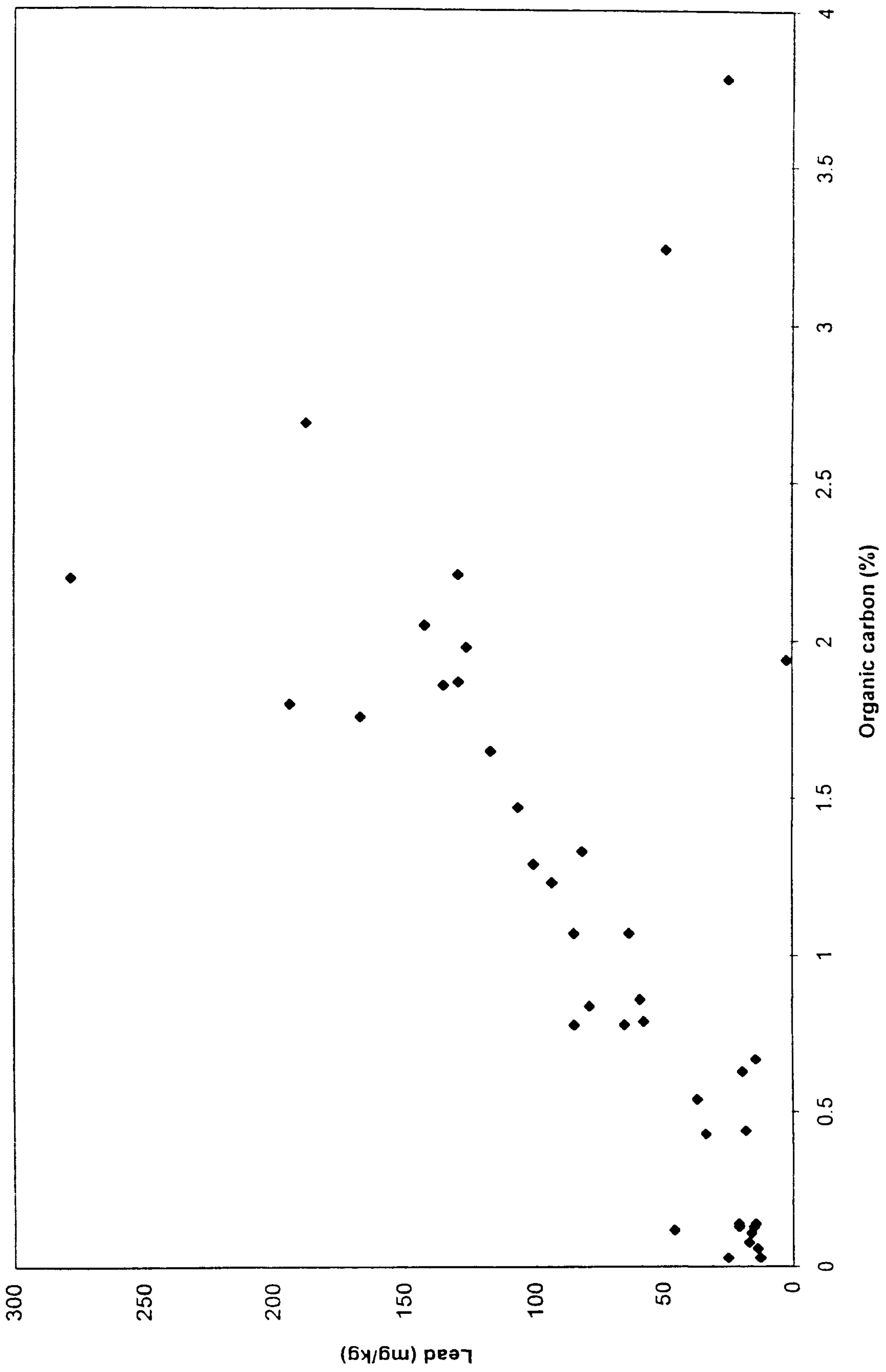


Figure A5.6 The relationship between lead and median particle diameter in sediments from the Mersey estuary.

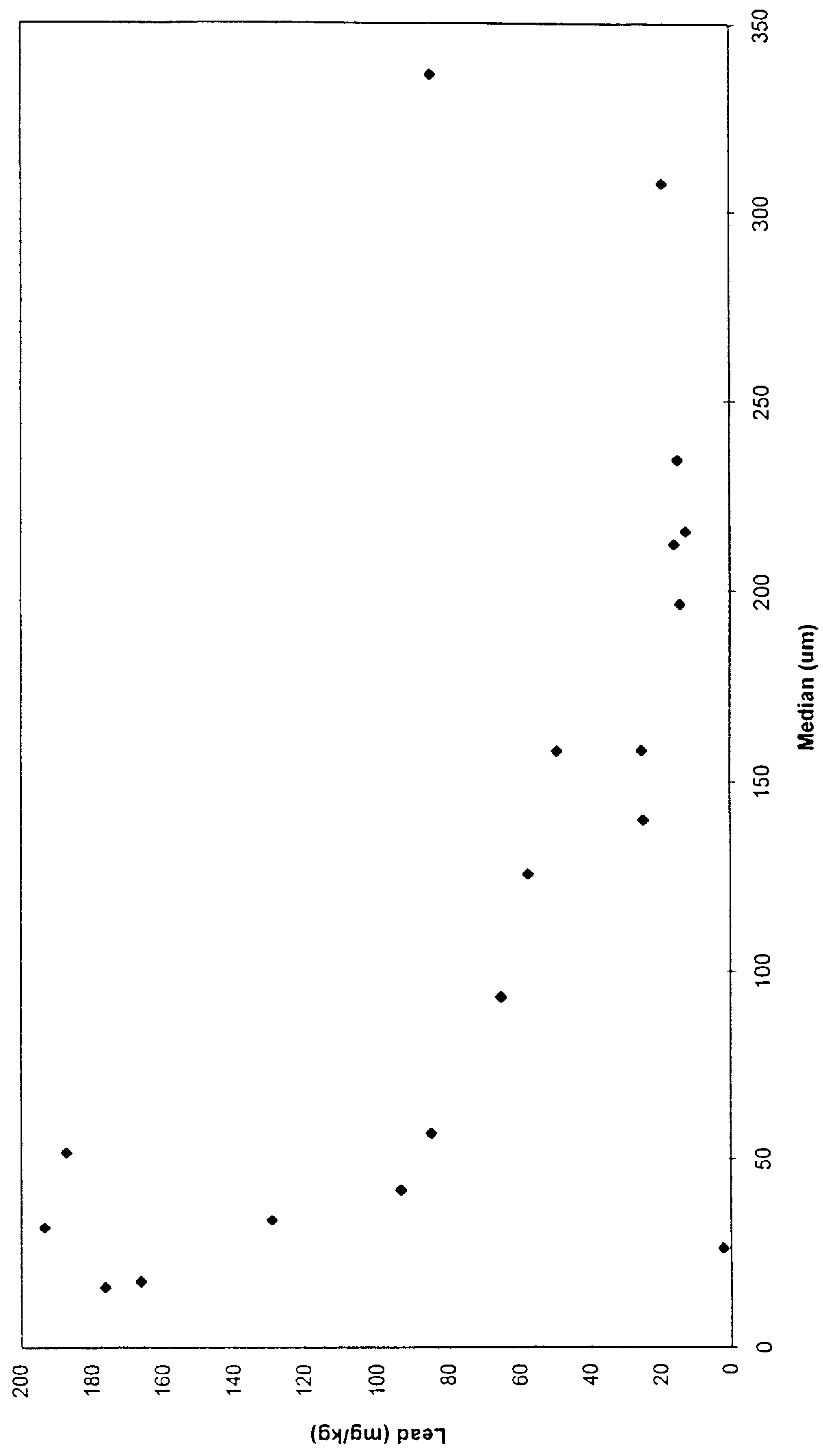


Figure A5.7 The relationship between mercury and organic carbon in sediments from the Mersey estuary.

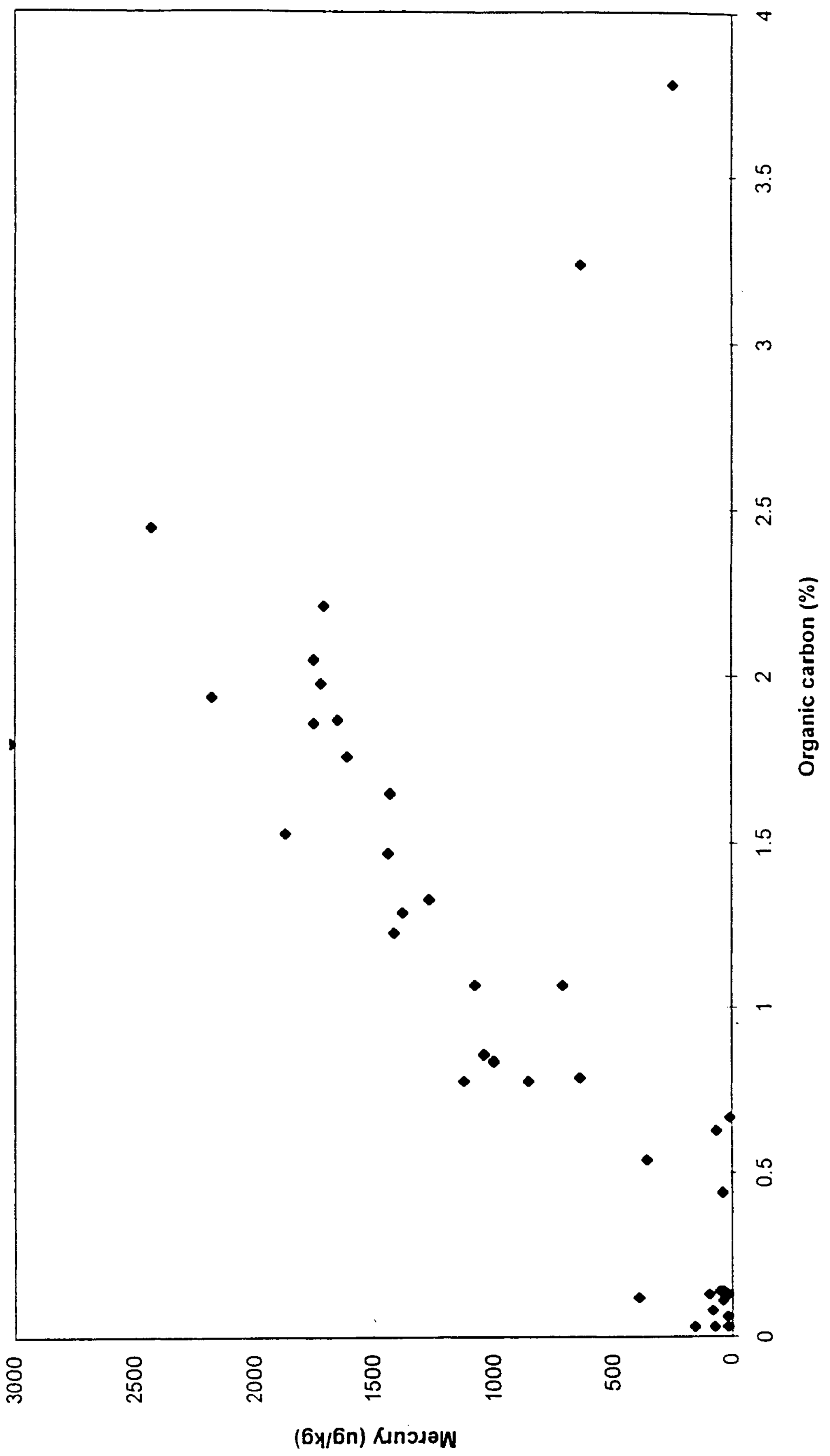


Figure A5.8 The relationship between lead and aluminium in sediments from various estuaries.

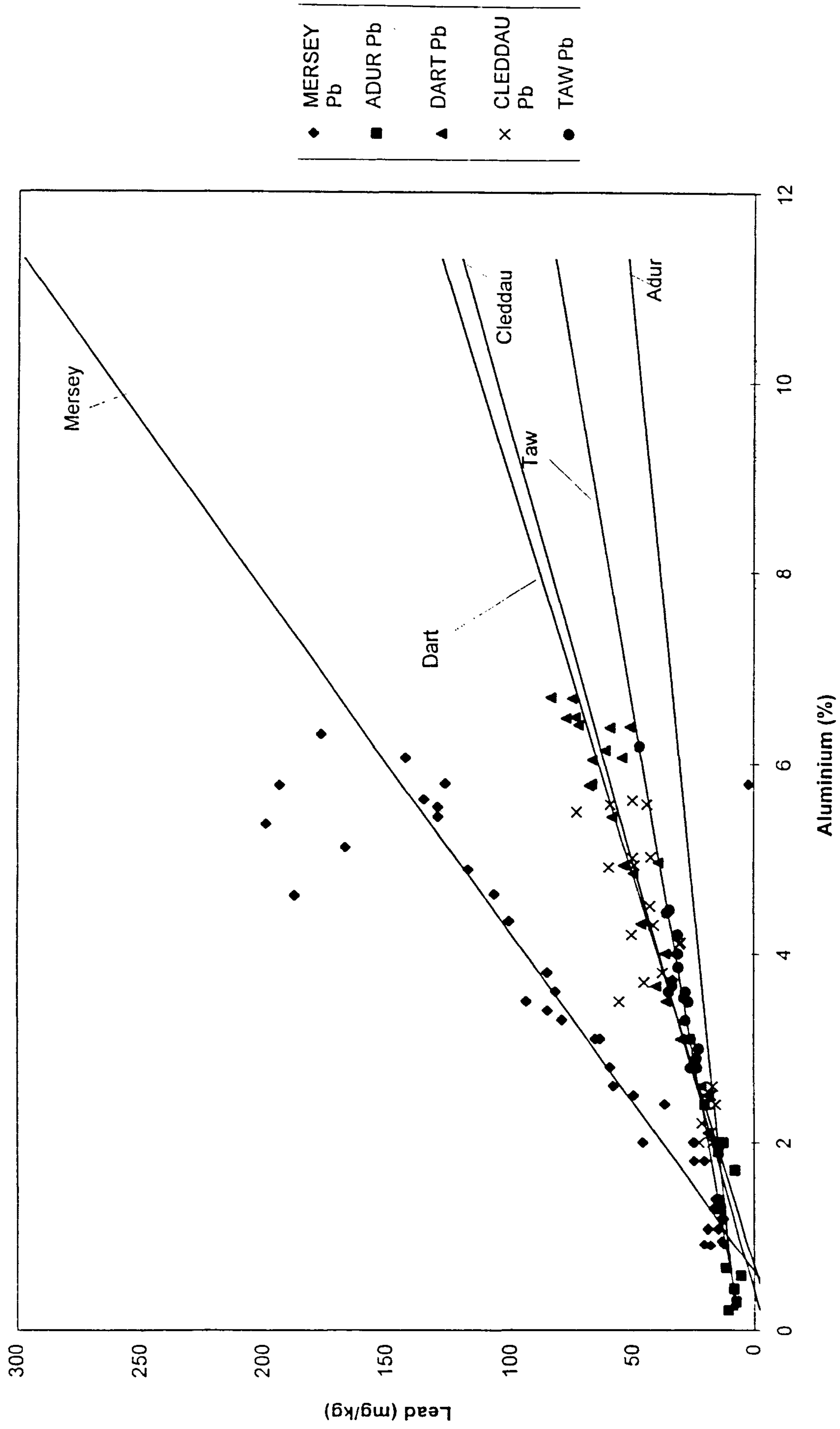
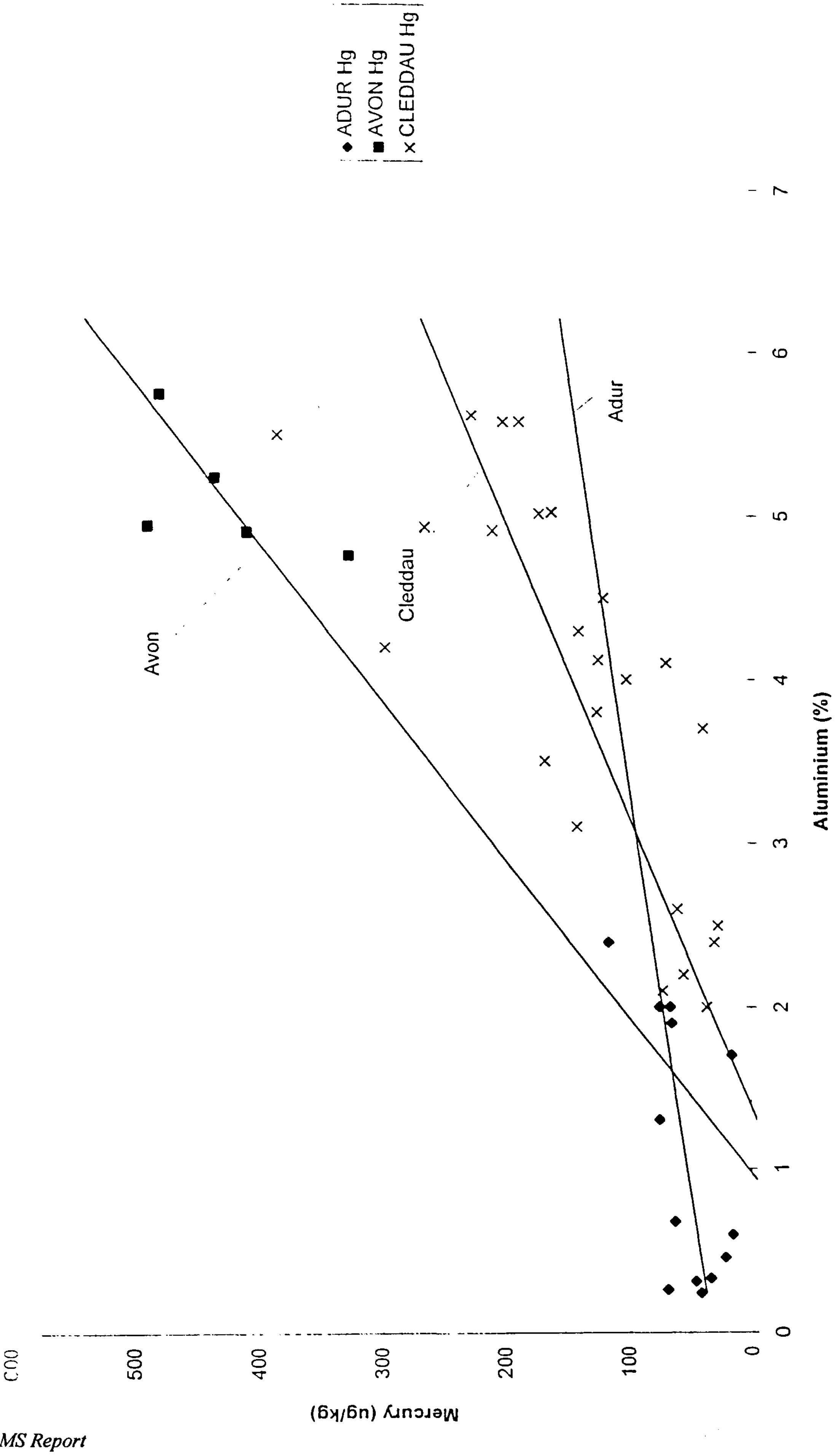


Figure A5.9 The relationship between mercury and aluminium in sediments from various estuaries.



ANNEX 6

STANDARD OPERATING PROCEDURES

Analytical procedures for the determination of organochlorine pesticides, polychlorinated biphenyls and polycyclic aromatic hydrocarbons in sediments

At the 1995 meeting of the Working Group on Marine Sediments in Relation to Pollution it was agreed to review standard operating procedures for organochlorine pesticides and PCBs as well as for polycyclic aromatic hydrocarbons. Method descriptions were received from four institutes (organochlorine compounds) and two institutes (PAHs), respectively. Additional information was submitted concerning the analysis of polychlorinated dibenzo-*p*-dioxins and -furans as well as of planar CBs.

Analyses of organic compounds include several steps:

- extraction of dry or wet sediment samples with organic solvents,
- clean-up steps in order to remove co-extracted components interfering with subsequent analyses,
- possibly a separation of the cleaned-up extract into different fractions by column chromatography,
- chromatographic separation (GC, HPLC) with subsequent detection of compounds (e.g., ECD, fluorescence detector).

All steps can contribute to the overall error in measurement. The QUASIMEME 1995 (round 4) exercises demonstrate that there are still considerable difficulties in analysing organic contaminants reliably. The determination of organochlorine pesticides (OCPs) was more difficult than for CBs: the variances for OCPs ranged from 23 to 118 %, for CBs from 20–35 %. For PAHs, between-lab variances observed in the QUASIMEME exercise 1995 (round 4) are similar for standard solutions, cleaned and raw sediment extracts: 13–22 %, 17–26 % and 17–34 %, respectively.

For all steps, various procedures can be applied. The choice of an appropriate procedure for the sample matrix under investigation might be very important. F. Smedes and J. de Boer discussed the advantages and disadvantges of several methods for the determination of chlorobiphenyls in detail (Smedes, F., and de Boer, J. In press. Chlorobiphenyls in marine sediments: Guidelines for determination. ICES Techniques in Marine Environmental Sciences No. 21). Most of the methods reviewed are appropriate to other organochlorine compounds, too. For the analyses of polycyclic aromatic hydrocarbons such an overview is not available.

In the following, the main steps of the procedures reported by participants of the WGMS are summarized. Polychlorinated dibenzo-*p*-dioxins and -furans and planar CBs are not included. They require more complex clean-up procedures.

The letters a) to d) refer to members of WGMS who submitted information:

a) Ian Davies, SOAEFD Marine Laboratory, P.O. Box 101, Victoria Road,
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b) Bernard Boutier, IFREMER Nantes, BP 1049, 44037 Nantes Cedex 01, France
c) Birgit Schubert, Federal Institute of Hydrology, P.O. Box 309, 56003 Koblenz, Germany
d) Teresa Nunes, Institut Español de Oceanografia, CO de Vigo, Apartado 1552,
36280 Vigo, Spain

DETERMINATION OF ORGANOCHLORINE COMPOUNDS AND PCBS IN SEDIMENTS

Storage of sediment samples:
a) no information
b) no information
c) frozen (–20 °C) or freeze-dried for long-term storage
d) frozen (–20 °C) or freeze-dried for long-term storage

Drying procedure (if applicable):
a) no information
b) no information
c) freeze-drying
d) freeze-drying

Further sample preparation:
a) grinding and sieving of sediments
b) no information
c) sieving (<2 mm: dry sieving; '<20 µm + residual TOC': wet sieving with ultrasonic treatment and further separation by different settling velocities); grinding of each fraction
d) sieving to 2 mm and grinding

Extraction procedure:
a) hot Soxhlet; cellulose thimbles; 4 hr (small thimbles), 8 hr (large thimbles);
methyl t-butyl ether
b) Soxhlet; 16 hr
hexane/acetone (50/50, vol/vol)
c) regular Soxhlet; 6 hr; fritted-glass thimbles;
hexane/acetone (2/1; vol/vol)
d) soxhlet; 15–20 hr; fritted-glass thimbles
pentane/dichloromethane (50/50; vol/vol)

Quantity of material extracted:
a) clean offshore marine sediment: 50–200 g
coastal or estuarine sediment: 30–50 g
sludges or spoils: 1–10 g
b) no information
c) depending on the expected contaminant concentrations and the grain-size
fraction analysed: 2–40 g
d) clean offshore marine sediment: 50 g
coastal or estuarine sediment: 10–50 g

Clean-up:
a) Refluxing each 2 g of sediment with 10 to 15 g of activated copper powder during extraction (removal of sulphur)
For removal of lipids, pigments, etc., and fractionation a column clean-up with 3 subsequent steps is carried out. The sample is in 1 ml hexane.
1 (Na_2SO_4) / 6 g of Al_2O_3 (5% H_2O); elution with hexane.
2 (Na_2SO_4) / 3 g of Al_2O_3 (5% H_2O); partial separation of pesticides from CBs.
3 (Na_2SO_4) / SiO_2 (3% H_2O); further fractionation, elution with hexane.
b) concentrated H_2SO_4, Hg and copper powder
c) Refluxing the extract with activated copper powder (sulphur removal).
For column clean-up, the sample is in 1 ml hexane:
- (Na_2SO_4) / SiO_2 (activated) for samples with a low TOC; elution with hexane/acetone (95/5; vol/vol)
- (Na_2SO_4) / Al_2O_3 (9% H_2O) for all samples, especially for removing lipid; elution with n-hexane concentrated H_2SO_4, if chromatographic clean-up was not sufficient
- fractionation with (Na_2SO_4) / SiO_2 (activated), if required; fraction 1: elution with n-hexane CBs and some pesticides; fraction 2: elution with n-hexane/acetone (95/5; vol/vol); other pesticides

d) Treatment with tetrabutyl ammonium/Na_2SO_3 (sulphur removal)
For column clean-up, the sample is in 3 ml pentane:
- Al_2O_3 (6 % water); elution with pentane; change of solvent to iso-octane (1 ml)
- fractionation with SiO_2 (1% H_2O): fraction 1: elution with iso-octane; CBs and some pesticides; fraction 2: elution with iso-octane/diethylether (85/15; vol/vol); other pesticides
- Fraction 2 is further cleaned-up with conc. H_2SO_4 when needed.

Internal standard:
a) CB 209, added to the extraction thimble
b) CB 209 prior to GC analysis
c) CB 103 prior to clean-up; tetrachloronaphthalene is added when the final volume for GC analysis is adjusted.
d) CB 155 added to the final extract just before GC analysis

Concentration of solvents:

a) rotary evaporator: slow evaporation to the approximate volume required or to less than 10 ml
  - Zymark turbovap: automatic evaporation from large volumes to 0.5 ml
  - blow down with a stream of air cleaned with charcoal

b) no information

c) Rotary evaporator: evaporation to a minimum volume of 10 ml. Before blowing down with N_2 (5.0), a solution of dodecane is added as keeper.

d) Rotary evaporator, adding isooctane as keeper: evaporation to a minimum volume of 3–5 ml. Further concentration with N_2 (5.0).

Storage of sample extracts:

a) raw extract: in dichloromethane or n-hexane (methyl t-butyl ether has to be replaced); in refridgerator or metal cupboard
cleaned-up extract: in hexane or 2,2,4-trimethylpentane; in refridgerator or cupboard

b) no information

c) raw and cleaned-up extracts: in hexane/acetone, hexane or 2,2,4-trimethylpentane; in cupboard at room temperature

d) cleaned-up extracts in iso-octane in the refridgerator for a short period (< 1 month)

Calibration:

a) set of 6 standards: 4, 10, 40, 100, 400, 1000 ng/g;
linear regression for the linear range

b) no information

c) set of 10 standards prepared from crystalline compounds: 1, 2.5, 5, 10, 20, 50, 100, 200, 400, 600 ng/ml (storage in a cupboard);
non-linear regression; peak height

d) multilevel calibration with at least 5 concentration levels; standards (stock solutions, intermediate solutions and working standards) prepared by weight. Stock solutions are prepared from crystalline compounds;
linear regression; peak height

GC conditions:

a) CP-Sil 8; no further information

b) DB 5 (60 m; 0.25 mm int. diameter; 0.2 μm film thickness)
automatic splitless injection (270 °C); ECD (300 °C);
carrier gas: H_2
temperature program:
  80 °C for 2 min
  to 200 °C with 20 °C/min; 200 °C for 20 min
  to 300 °C with 5 °C/min

c) DB 1 and DB 1701 in parallel (each: 60 m; 0.25 mm int. diameter; 0.25 μm film thickness)
automatic splitless injection (260 °C); ECD (300 °C);
carrier gas: He
temperature program:
  60 °C for 4 min
  to 150 °C with 8 °C/min; 150°C for 3 min
  to 230 °C with 4 °C/min; 230 °C for 30 min
  to 280 °C with 3 °C/min; 280 °C for 30 min

d) CP-Sil 8 and CP-Sil 19 in parallel (each 50 m)
automatic splitless injection
carrier gas: H_2

Analytical quality assurance:

a) in each batch:
  A set of 6 standards is run before each batch.
  method blank
  A laboratory reference sediment is treated as a sample.
  duplicate analyses of one sediment sample

b) no information

c) in each batch:
  A set of 10 standards is run before each batch.
  method blank

A laboratory reference sediment is treated as a sample.
determination of the recovery starting from the clean-up with a standard solution
(certified) reference materials: 2 to 4 times/year

d) For GC-measurement in each batch:
   discard of the first injection
   method blank
   at least 5 working standards placed between samples

   For the complete procedure, each batch includes a method blank. Every second batch, a recovery check starting in the clean-up step with a standard solution is carried out. A reference material (HS-1, NRC, Canada) is included every month. About 15 % of the samples analysed are replicates.

Calculations

a) no information
b) no information
c) Peak heights are corrected for the peak height of the internal standard tetrachloro-naphthalene (TCN). Correction for the recovery of the clean-up procedure. The recovery is determined with standard solutions treated as samples.
d) Peak heights are corrected for the peak height of the internal standard, CB 155.
   Sample extract weights and internal standard weights are used in the calculations; all CBs and pesticide concentrations are expressed by weight.

DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN SEDIMENTS

Drying procedure (if applicable):

b) no information

c) freeze-drying

Further sample preparation:

b) no information

c) sieving (<2 mm: dry sieving; '<20 µm + residual TOC': wet sieving with ultrasonic treatment and further separation by different settling velocities); grinding of each fraction

Extraction procedure:

b) Soxhlet; 16 hr
   dichloromethane/acetone (50/50, vol/vol)

c) regular Soxhlet; 6 hr;
   fritted-glass thimbles; hexane/acetone (2/1; vol/vol)

Quantity of material extracted:

b) no information

c) depending on the expected contaminant concentrations and the grain-size fraction analysed: aliquot corresponding to 0.16 to 3.2 g

Clean-up:

b) SiO_2 column (SEP-PAK)

c) For column clean-up, the sample is in 1 ml hexane/acetone:
   - (Na_2SO_4) / SiO_2 (activated) / cyanopropyl phase; alternatively:
   - (Na_2SO_4) / Al_2O_3 (9% H_2O), especially when samples contain high concentrations of coloured organic compounds.

Internal standard:

b) phenanthrene-d10; benzo(*ghi*)fluoranthene
c) 6-methylchrysene is added prior to clean-up; benzo(*b*)chrysene is added when the final volume for GC analysis is adjusted.

Concentration:

b) no information

c) rotary evaporator: evaporation to a minimum volume of 10 ml
blow down with N_2 (5.0) to small volumes (0.5 or 1 ml)

Storage of sample extracts:

b) no information

c) raw and cleaned-up extracts: in hexane/acetone, hexane or acetonitrile; in cupboard at room temperature

Calibration:

b) no information

c) set of 7 standards prepared from crystalline compounds: (storage in a cupboard)
linear regression; peak height

HPLC conditions:

b) HPLC with a wavelength programmable fluorescence detector:
Vydack 201 TP (reversed phase; int. diameter: 4.6 mm; length: 25 cm)
automatic injection: 10 µl
temperature of column oven: 30 °C
mobile phase: acetonitrile/water (%):
0 min: 50/50; 5 min: 55/45; 16 min: 55/45; 40 min: 74/26; 50 min: 90/10

wavelength program:	excitation/emission in nm
fluoranthene, benzo(*b*)fluoranthene:	260 / 420
benzo(*k*)fluoranthene, benzo(*a*)pyrene, benzo(*ghi*)perylene	290 / 430
indeno(123-*cd*)pyrene:	300 / 500

c) HPLC with a wavelength programmable fluorescence detector:
MZ-PAH C18, (MZ Analysentechnik, Mainz; particle size: 5 µm; int. diameter: 3 mm; length: 25 cm)
automatic injection: 10 µl
temperature of column oven: 35 °C
mobile phase: acetonitrile/water (%):
0 min: 60/40; 35 min: 100/0; 55 min: 100/0; 60 min: 60/40

wavelength program:	excitation/emission in nm:
naphthalene, fluorene, phenanthrene:	275 / 350
anthracene:	375 / 425
fluoranthene, pyrene:	335 / 440
benz(*a*)anthracene, chrysene	315 / 405
benzo(*e*)pyrene, benzo(*b*)fluoranthene	330 / 420
benzo(*k*)fluoranthene, benzo(*a*)pyrene	375 / 460
dibenz(*ah*)anthracene, benzo(*ghi*)perylene:	345 / 420
indeno(123-*cd*)pyrene	300 / 500

Analytical quality assurance:

b) no information

c) in each batch:
set of 7 standards is run before each batch
method blank
a laboratory reference sediment is treated as a sample
reference materials (SRM 1941; SRM 1647 c; NIST)
determination of the recovery of the clean-up step

ANNEX 7

GUIDELINES FOR THE DETERMINATION OF CHLOROBIPHENYLS IN SEDIMENTS: ANALYTICAL METHOD

These guidelines take into account the papers from Smedes and de Boer [1, 2].

Introduction

These guidelines are extracted from the review paper written by Smedes and de Boer [1] on request of ICES. For more detailed explanations, it is advisable to consult this paper.

The analysis of chlorinated biphenyls in sediments generally includes extraction with organic solvents, clean-up, removal of sulphur, column fractionation and gas chromatographic separation, mostly with electron capture or mass-spectrometric detection. All of the steps in the procedure are susceptible to insufficient recovery and/or contamination. Where possible, quality control procedures are recommended in order to check the method performance. In addition, the quality control aspects relating to calibrant, extraction, clean-up, etc., are considered. These guidelines are intended to encourage and assist analytical chemists to critically (re)consider their methods and to improve their procedures and/or the associated quality control measures where necessary. It should be noted that these guidelines do not cover the determination of non-*ortho* substituted CBs. Due to the low concentrations of non-*ortho* CBs in sediments compared to those of other CBs, their determination requires an additional separation and concentration step.

These guidelines can also be applied for the analyses of several organochlorine compounds, e.g., chlorobenzenes or DDT and its metabolites, and hexachlorocyclohexanes. The recovery in the clean-up procedures has to be checked carefully. Especially treatment with H_2SO_4 results in loss of, e.g., dieldrin and endosulfanes. Also, the clean-up procedure with silver ions can result in low recoveries for special pesticides.

It is neither possible nor desirable to provide fully detailed guidelines for the analysis of sediments. If necessary, guidance should be sought from highly specialized research laboratories. Whichever procedure is adopted, each laboratory must demonstrate the validity of each step of their procedure. In addition, the use of a second, different method, next to the routine procedure, is recommended as a validation. The analyses have to be carried out by experienced staff.

Sampling and storage

Plastic materials (except polyethylene or polytetrafluorethene) must not be used for sampling due to adsorption by the container material.

The samples should be transported in closed containers; a temperature of 25 °C should not be exceeded. If the samples are not analysed within 48 hours after sampling, the sample has to be stored at 4 °C (short-term storage). A storage over several months is only possible for frozen (below –20 °C) and dried samples.

Blanks and contamination

The procedural detection limit is determined by the blank value. In order to keep the blank value as low as possible, all glassware, solvents, chemicals, adsorption materials, etc., should be free of CBs or other interfering compounds.

- Glassware should be extensively washed with detergents and heated at >250 °C and rinsed with organic solvent prior to use.

- All solvents should be checked for impurities by concentrating the volume normally used in the procedure to 10% of the normal end volume. The presence of CBs and other compounds in the solvents can then be checked by GC analysis.

- All chemicals and adsorption materials should be checked for impurities and purified (e.g., by heating or extraction), if necessary. Glass fiber Soxhlet thimbles should be pre-extracted. The use of paper thimbles should be avoided. Alternatively full glass Soxhlet thimbles, with a G1 glass filter at the bottom can be used. The storage of these super-cleaned materials for a long period of time is not recommended, as laboratory air can contain CBs that will be absorbed by these materials. Blank values occurring despite all the above-mentioned precautions may be due to contamination from the air.

Pre-treatment

CBs can be extracted from wet or dried samples. However, storage, homogenization and extraction are much easier when the samples are dry. Drying of the samples may alter the concentration, e.g., by loss of compounds through evaporation or contamination.

Before taking a subsample for analysis, the sample should be sufficiently homogenized.

Chemical drying of samples can be performed by grinding with Na_2SO_4 or $MgSO_4$ until the sample reaches a sandy consistency. It is essential that between grinding and extraction at least several hours are taken to allow a proper binding of the water to avoid insufficient extraction.

Freeze drying is becoming a more popular technique. Losses through evaporation are diminished by keeping the temperature in the evaporation chamber below 0 °C. Losses and contamination have to be checked. Contamination during freeze drying is reduced by putting a lid on the sample container with a hole of about 3 mm in diameter.

Extraction

The target compounds have to be extracted from the sediment with an organic solvent prior to further analysis.

Wet sediments are extracted by mixing with organic solvents. Extraction is stimulated by shaking, Ultra Turrax mixing, ball mill tumbler or ultrasonic treatment. Water miscible solvents are used, especially in the first step, such as methanol, acetone, acetonitrile, etc. The extraction efficiency of the first step is low as there will be a considerable amount of water in the liquid phase. The extraction is continued with a mixture of polar and apolar solvents (acetone + hexane or methanol + dichloromethane). For an accurate extraction, at least three subsequent extractions are needed and the contact time (24 hours) with the solvent should be sufficient to complete the desorption of the CBs from the sediment.

Wet sediments can also be extracted utilizing a Soxhlet but this is best done in two steps. First a polar solvent, such as acetone, is used to extract the water from the sediment. Then the flask is replaced and the extraction is continued with a mixture of, e.g., acetone/hexane.

In both cases, water has to be added to the extracts and the CBs have to be extracted to an apolar solvent such as hexane.

For dried sediments, Soxhlet extraction is the most frequently applied technique to extract CBs. The use of a mixture of a polar and an a polar solvent (e.g., acetone/hexane) is recommended for sufficient extraction efficiency. A good choice is 25% acetone in hexane. A higher content of the polar solvent increases the extraction efficiency, but the polar solvent has to be removed prior to gas-chromatographic analysis. The extraction can be carried out with a regular Soxhlet or a hot Soxhlet. At least 50–60 extraction cycles have to be performed (~ 8 hours for the hot Soxhlet). The extraction efficiency has to be checked for different types of sediments by a second extraction step. These extracts should be analysed separately.

Supercritical fluid extraction (SFE) is a relatively new method. The optimum conditions are still under investigation. A new static extraction system applying high temperature and high pressure seems to be a promising technique.

All of the methods described are, in principle, suitable for the extraction of CBs from sediments. However, for dry samples Soxhlet extraction is recommended over mixing methods.

Prior to any concentration step a keeper (high boiling alkane) has to be added.

Clean-up

The crude extract requires a clean-up as many other compounds are co-extracted. This extract will be coloured due to chlorophyll-like compounds extracted from sediment, and it will also contain sulphur and sulphur-containing compounds, oil, PAHs and many other natural and anthropogenic compounds.

a) Removal of sulphur and sulphur-containing compounds

An aqueous saturated NA_2S0_3 solution is added to a hexane extract. In order to allow transfer of the HSO^{3-} ions to the organic phase, tetrabutylammonium (TBA) salts and isopropanol are added to the mixture. Subsequently, water is added to remove the isopropanol. The aqueous phase is quantitatively extracted with hexane [3]. If the extraction was performed by a polar solvent miscible with water, a Na_2SO_3 solution can be added directly after the extraction. If the extraction mixture also contains an apolar solvent, then depending on the ratio of the solvents, the addition of TBA and isopropanol is not necessary. Any excess of Na_2SO_3 and reaction products can be removed by addition of water and partitioning between apolar solvent and water.

Japenga *et al.* [4] developed a column method for the removal of sulphur and sulphur-containing compounds. The column material is made by mixing an aqueous solution of Na_2SO_3 with Al_2O_3. Some NaOH was also added to improve the reaction with sulphur. Subsequently, the material is dried under nitrogen until a level of deactivation equivalent to 10 % water is reached. Storage must be under nitrogen as sulphite in this form may easily be oxidized to sulphate. Eluting the extract (hexane) through a column filled with this material results in removal of the sulphur in combination with further clean-up of the sediment extract. The sulphur removal properties are somewhat difficult to control.

Mercury, copper powder, wire or gauze remove the sulphur directly from an organic solvent. Although mercury is appropriate for removing sulphur, it should be avoided for environmental reasons. Copper can be applied after or during Soxhlet extraction. Ultrasonic treatment might improve the removal of sulphur. If sulphur appears to be present in the final extract, the amount of copper or mercury was insufficient and the clean-up procedure has to be repeated.

Silver ions strongly bind sulphur and sulphur compounds. Loaded on silica, $AgNO_3$ is a very efficient sulphur removing agent. It can be prepared by mixing dissolved $AgNO_3$ with silica and subsequently drying under nitrogen. Compounds containing aromatic rings are strongly retained, but for CBs this retention is reduced, probably due to shielding of the rings by the chlorine atoms. Retained compounds can easily be eluted by using cyclohexene, or another solvent with double bonds, as a modifier.

Elemental sulphur is strongly retained on a polystyrene divinylbenzene copolymer column as generally applied for gel permeation chromatography (GPC). In addition, this method combines the removal of sulphur with a clean-up.

All of these methods have their advantages and disadvantages. Sometimes for different samples the use of multiple methods may prove necessary. Several methods leave some aromatic sulphur compounds in the extract which will elute from the GC column at the same retention time as the lower CBs. The major part of these compounds can be removed by eluting an apolar extract over a column with silica loaded with concentrated sulphuric acid.

b) Further clean-up

As CBs are apolar, clean-up using normal phase chromatography is the most appropriate technique for their isolation from other compounds. Using an apolar solvent, e.g., hexane or iso-octane, as an eluent, CBs normally elute very rapidly. All polar solvents used in the extraction or sulphur removal step should be removed before further clean-up. The last concentration step is usually performed by evaporation with a gentle stream of nitrogen. Evaporation to dryness should always be avoided.

Deactivated Al_2O_3 (5–10% water) is used very often as a primary clean-up. Provided that sulphur has been removed, Al_2O_3 normally gives a sufficiently clean extract for a GC-ECD screening of the sample.

Deactivated SiO_2 (1–5 % water) does not retain CBs (including planars) and only slightly retains polyaromatic hydrocarbons when eluted with hexane or iso-octane.

For high activity silica (overnight at 180 °C) the retention of CBs is negligible while PAHs are more strongly retained. The CBs and a few organochlorine compounds are eluted with apolar solvents. Using more polar solvents, some interfering organochlorine pesticides are eluted (e.g., hexane/acetone).

When GPC is applied for removing the sulphur, the removal of high molecular weight material can be incorporated into the procedure as well. GPC does not separate CBs from other compounds in the same molecular range such as organochlorine pesticides and so additional clean-up is usually required.

For the separation of CBs from lipids or oil components, reversed phase HPLC can be used. Because of the aqueous solvents in reversed phase HPLC, the samples have to be transferred several times between polar and apolar solvents.

Gas chromatography (GC)

Because of the large number of CB congeners (209), high resolution capillary GC is the method of choice for the determination of CBs. The CB analysis of sediments should focus on the determination of selected individual congeners. As it is currently impossible to separate all CBs in technical mixtures and to separate them from other ECD detectable compounds, it is recommended that two columns of different selectivity (polarity) be used for analysis. For more reliable separation of CBs, multidimensional GC (MDGC) is the preferred method. This technique is especially valuable for specific separations, but still needs basic investigations before routine application is possible. For all GC methods, parameters have to be optimized.

Column diameters

Column dimensions for the determination of CBs should be the following:

- length: minimum 50 m
- inner diameter: maximum 0.25 mm
  More resolution can be obtained by reducing the inner diameter to 0.20 mm or less. Below a diameter of 0.15 mm the carrier gas pressure rises to values greater than 500 kPa, which are not compatible with normal GC equipment. Also the risk of leakages increases.
- film thickness: between 0.2 and 0.4 μm.

Stationary phases

A wide range of stationary phases can be used for the separation of CBs (e.g., 94% dimethyl-, 5% phenyl-, 1% vinyl polysiloxane, or 7% phenyl-, 7% cyanopropyl-, 86% methyl siloxane). The use of more polar phases is sometimes limited as their maximum temperature is not as high as for apolar, chemically bonded phases. Stationary phases that separate CBs on the basis of molecular size, such as the liquid crystal phase, should not be used for monitoring purposes since they do not provide sufficient reproducibility.

Carrier gas

Preferably hydrogen should be used as the GC carrier gas. When using columns with very small inner diameters, the use of hydrogen is essential. The linear gas velocity should be optimized. Appropriate settings for 0.25 mm i.d. columns range from 20–40 cm/s and for 0.15 mm i.d. columns from 30–50 cm/s.

Injection techniques

The two systems commonly used are splitless and on-column injection. Split injection should not be used because strong discrimination effects may occur. Other techniques such as temperature-programmed or pressure-programmed injection may have additional advantages, but should be thoroughly optimized before use. The volume of the liner should be large enough to contain the gas volume of the evaporated injected solvent. When the liner is too small, memory effects can occur due to contamination of the gas tubing attached to the injector. Very large liner volumes can cause a poor transfer of early eluting components, so that peaks due to those analytes will be reduced or even disappear. An auto-sampler should be used. In addition, the use of a light packing of (silylated) glass wool in the liner does improve the response and reproducibility of the injection, but some organochlorine pesticides like DDT may be degraded when this technique is applied.

Temperature programming

The temperature programme has to be optimized for a sufficient separation of the CB congeners. An analysis time of 60–120 minutes is inevitable. Besides a reproducible temperature programme, a fixed equilibration time is important for a correct analysis and constant retention times.

For further details and recommendations, the paper by Smedes and de Boer [1] should be consulted.

Detection

The most frequently used detector for CB analysis is the electron capture detector (ECD). Injection of chlorinated or oxygen-containing solvents should be avoided. The use of a mass selective detector (MSD) or even a mass spectrometer (MS) as a detector for CB analysis is becoming more common and generally applicable. Negative chemical ionization (NCI) is extremely sensitive for penta- to deca-chlorinated CBs (ca. ten fold better than ECD).

Electron impact ionization (EI) may be used as an alternative ionization method, but for most CBs the sensitivity of this method is ten-fold lower than for ECD.

Identification

The presence of a single compound of CBs is proved if the retention time of the substance corresponds with that of the respective compound in the standard solution analysed under the same conditions on both columns. Using a GC/MS system additionally the molecular mass or characteristic mass fragments (chlorine cluster) is a suitable way to prove the identification of the CBs.

Quantification

Since the ECD has a non-linear response curve, a multilevel calibration with at least five concentration levels is strongly recommended. A point-to-point calibration is preferred. If that option is not available, a linear working range can be identified, which allows the use of linear regression within this range. Alternatively, a non-linear fit can be used. In case that regression is applied, the standards should always be recalculated as samples and checked against their nominal values. Deviation from the nominal values should not exceed 5 %.

When the chromatogram is processed by using automated integrators, the baseline is not always set unambiguously, and always needs visual inspection. The use of peak heights is recommended for quantification.

The GC system should be equilibrated by injecting at least one standard or sample omitting any further evaluation prior to a series of samples and standards. In addition, standards used for multilevel calibration should be regularly distributed over the sample series, so matrix and non-matrix containing injections alternate. A sample series should consist of

- a procedural blank
- a laboratory reference material
- at least 5 standards
- one standard solution that has been treated similarly to the samples (recovery determination).

Using a GC/ECD system with two columns of different polarities, the more reliable result has to be reported.

The limit of determination should depend on the purpose of the investigation. A limit of 0.1 ng/g (dry weight, fraction < 2 mm) or better should be achieved. The method for calculating the limit of determination should be according to QUASIMEME advice. The limit of determination that can be achieved depends on the blank, on the sample matrix, concentrations of interfering compounds and the intake of sediment for analysis.

Quality assurance

A number of measures should be taken to ensure a sufficient quality of the analysis. Five main areas can be identified:

- internal standards
- extraction efficiency and clean-up
- calibrants and calibration
- system performance
- long-term stability

Internal standards

The ideal internal standard is a CB which is not found in the samples and does not co-elute with other CBs, e.g., CBs 29, 112, 155, 198 or all 2,4,6-substituted CB congeners. Alternatively, 1,2,3,4-tetrachloronaphthalene can be used.

Extraction and clean-up

The check of extraction and clean-up can be performed by analysing a reference material. For the check of the clean-up and concentration steps, it is recommended to pass a standard solution through the whole procedure. This standard solution is used for the determination of the recovery for the sample series. Additionally, an internal recovery standard should be added to each sample before extraction, to check for recovery during the analytical procedures. If major losses have occurred, then the results obtained should not be reported. CB 29 is suggested as a recovery standard, as, because of its high volatility, losses due to evaporation are easily detected. CB 29 elutes relatively late from alumina and silica columns. Small peaks that may be present in the gas chromatogram at the retention time of CB 29 do not hinder the use of this CB because the recovery standard only indicates major errors in extraction or clean-up.

In case GC/MS is applied, labelled CBs can be used as recovery standards. This allows correction for recovery, provided that each chlorination stage is represented.

Calibrants and calibration

CB determinations should always be carried out using calibration solutions prepared from crystalline CBs. Preferably certified CBs should be used. Two independent stock solutions of different concentrations should always be prepared simultaneously to allow a cross check to be made. Calibration solutions should preferably be stored in ampoules in a cool and dark place. For all containers with standards, the weight loss during storage should be recorded.

After clean-up and before GC analysis, at least one internal standard is added for volume correction.

Internal standards should be added in a fixed volume or weighed to all standards and samples.

System performance

The performance of the GC system can be monitored by regularly checking the resolution of two closely eluting CBs. A decrease in resolution points to deteriorating GC conditions. The signal-to-noise ratio yields information on the condition of the detector. A dirty ECD-detector or MS-source can be recognized by the presence of a higher background signal, together with a reduced signal-to-noise ratio (see also detection).

Long-term stability

One laboratory reference sample should be included in each series of samples. A quality control chart should be recorded for selected CBs. If the warning limits are exceeded, the method should be checked for possible errors. When alarm limits are exceeded, the results obtained should not be reported.

A certified reference material should be analysed at minimum twice a year and each time the procedure is changed. Each laboratory analysing sediments should also participate in interlaboratory studies on the determination of CBs in sediments on a regular basis.

References

[1] Smedes, F., and de Boer, J. In press. Chlorobiphenyls in marine sediments: Guidelines for Determination. ICES Techniques in Marine Environmental Sciences No. 21.

[2] Smedes, F., and de Boer, J. 1994. Guidelines for the determination of chlorobiphenyls in sediments. Quimica Analytica, 13: 100–108.

[3] Jensen, S., Renbey, L., and Reutergårdh, L. 1977. Residue analysis of sediment and sewage sludge for organochlorines in the presence of elemental sulfur. Anal. Chem., 49: 316–318.

[4] Japenga, J., Wagenaar, W.J., Smedes, F., and Salomons, W. 1987. A new rapid clean-up procedure for the simultaneous determination of different groups of organic micropollutants in sediments; application in two European estuarine sediment studies. Environ. Techn. Lett., 8: 9–20.

ANNEX 8

TEMPORAL TRENDS IN SOME SEDIMENTS

1.1 Standards based on limited change

When waste is deposited at a disposal site and the material reaches the seabed, there will almost certainly be a change in the quality of the sediment at the seabed. This change is likely to be most pronounced in the early stages of an on-going operation; it will then reach an equilibrium. A standard based on limited change in this 'equilibrium' period will ensure that the quality of the seabed at the disposal site will not become worse.

1.2.1 Measuring change

The following section provides two examples of the approach to measuring change in sediment and setting 'no-change' standards.

1.2.2 Tyne

Introduction

In order to improve the water quality of the Tyne estuary, changes were made in the Tyneside sewerage system in the late 1970s. Among these, the installation of new collection sewers and treatment facilities has resulted in the production of quantities of primary settled sewage sludge which is deposited at sea off the River Tyne. The operation started at a low level in 1978 and increased to an annual deposition of approximately 500,000 wet tonnes in 1984, since when it has varied little.

The seabed at the sewage sludge disposal site consists of soft muddy sand and the water is 50 m deep. The tidal streams run approximately parallel with the coast, with maximum velocities of 40 cm s^{-1}.

During the early stages of operation, regular monitoring was undertaken with a view to detecting any effects of disposal as soon as they occurred. The monitoring programme was primarily aimed at assessing the condition of the seabed and its associated fauna, although the area was also examined for water and fish quality as part of nation-wide monitoring programmes. The present discussion deals with studies of spatial and temporal changes in surface sediment quality. The temporal component of this work has been carried out since 1987.

Methods

Seabed samples were collected in line with GCSDM guidelines. A 0.1 m^2 Day grab was used to sample the seabed. Immediately after collection, a surface scrape of the sediment was taken for bacterial analysis. *E. coli* were enumerated using a membrane filtration procedure.

Sub-samples of the surface 0–1 cm of the sediment were stored frozen for later chemical and physical analysis. On return to the laboratory, the sediments were defrosted and sieved at 63 µm to extract the fine fraction. The fines were subdivided and the carbon content of one sub-sample determined instrumentally, after pre-treatment with sulphurous acid to remove any carbonates present. Another sub-sample was digested with aqua regia and the metals mercury, copper, chromium, nickel, lead and zinc determined using atomic absorption spectrophotometry.

Results and Discussion

The area of sludge settlement as indicated by faecal bacteria is at and to the southeast of the disposal site (Figure A8.1). This figure also shows areas of sediment impacted by the outflow of the River Tyne and coastal outfalls, both of which contain sewage bacteria.

The examples given in Figures A8.2a to A8.2c show that there is a general reduction in trace metal and carbon concentrations with distance from the shore and that the outflow of the River Tyne affects sediment composition. However, with the possible exception of chromium, there is no evidence of accumulation of either metals or carbon at the disposal site. In the context of the riverine inputs to the nearshore zone, it should be noted that the Tyne drains a catchment which includes the heavily mineralized Pennines as well as industrial sources of contamination and the elevated levels of metals cannot be ascribed wholly to man-made contamination.

In order to assess any changes in sediment quality with time, a system has been set up based on a stratified random design (Figure A8.3) in which sediment samples collected in different years can be compared. The samples are collected from an area centred on the zone of initial settlement defined by the faecal bacteria discussed earlier and are designed to detect changes in sediment quality brought about if there is an accumulation of sludge. This design meets the requirements of GCSDM for a 'no-change' standard. This sampling system supersedes an earlier design based on transect sampling which was liable to reflect a component of the general offshore trend of decreasing metal concentrations.

For most elements there is little year-to-year variation in the results (Figure A8.4a–d).

1.2.3 Liverpool Bay

Introduction

Each year about 1.5 million wet tonnes of sewage sludge are deposited at a designated site in Liverpool Bay (Figure A8.5) by North West Water Ltd (formerly the North West Water Authority). The MAFF Burnham-on-Crouch Laboratory has studied the area since the 1970s to determine any effects on water, sediment or fish quality.

This work has included the analysis of sediment samples collected near the disposal site (Figure A8.5), where effects on sediment chemistry have been observed (Norton *et al.*, 1984 and unpublished data).

Methods

Sediment samples were collected using a 0.1 m^2 Day grab. Samples of the surface 0–1 cm of the sediment were stored frozen for later chemical and physical analyses. On return to the laboratory the sediments were defrosted and sieved to extract the fine fraction. While the 90 µm sieve was not in accord with GCSDM advice, it was used in preference to the 63 µm sieve to ensure consistency with earlier work.

The fines were subdivided and the carbon content of one sub-sample determined instrumentally, after pre-treatment with sulphurous acid to remove any carbonates present. Another sub-sample was digested with aqua regia and the metals mercury, copper, chromium, nickel, lead and zinc determined by atomic absorption spectrophotometry.

Results and Discussion

Concentrations of trace metals in the sediments exhibit highly non-normal distributions and are therefore described using non-parametric measures. Figure A8.6(a-c) shows the median and range of concentrations of mercury, zinc and chromium from 1980 to 1990. The most notable feature of the time series is the absence of any marked trend over the decade of study. Figure A8.6d shows carbon data presented in the same manner as the metal data. This shows a consistent median value during the period 1983 to 1990, although it appears that the concentrations may have been slightly lower in the early years of the decade. The concentration ranges show considerable overlap between all years suggesting that this small difference is of little significance.

When considering data from this sandy area, it must be recognized that the <90 µm fraction in general represents less than 5% of the total sediment and that, when considered on a whole sediment basis, the concentrations of metals are very low.

It is known that sediments in the vicinity of the disposal site contain higher concentrations of several metals (e.g., copper, mercury, zinc and lead) than sediments further away (Norton *et al.*, 1984) and it seems reasonable to conclude that there has been some accumulation of metal contaminants in the area as a direct consequence of the sewage-sludge disposal operation. However, the fact that there has been no increase during the last 10 years indicates that the system is in a steady state and has been so for at least the last decade.

1.2 No-change action levels

The above data show the changes in sediment metal concentrations at the Tyne and Liverpool Bay disposal sites. In order to show the data graphically, the Tyne data have been dealt with using parametric statistics while the Liverpool Bay data have required the use of non-parametric measures.

The Metals Task Team, after examining this information, together with some from the Garroch Head disposal site, decided that standards should be set on the basis of a Shewart chart using the standard errors calculated on the basis of five years' data. Two standard errors should be taken as the warning level and three as the Action Level. Figure A8.4 illustrates this approach in the case of the Tyne. These figures demonstrate that the sediment metal concentrations at the Tyne have not exceeded the 'no-change' action level. Of course, this approach is equally applicable to skewed data such as that from Liverpool Bay although it may be necessary to log-transform the data.

1.3 Calculation of 'no-change' standards

The following advice is provided to assist with the development of a 'no-change' standard using a control chart survey design:

1) The data should be as homogeneous as possible, i.e., it should have been derived from a consistent approach to sampling, preparation and analysis.

2) As the basic hypothesis is that conditions (i.e., metal concentrations) within the sampling unit are stable, the actual sampling format is immaterial. The important point is that the sampling strategy shall not have changed during the period of the study.

3) The points to be plotted on the control chart, and used for the establishing of the chart, should be the mean values of the metal concentrations for each of the surveys selected.

4) When establishing the chart, the data should be examined for any temporal trend, for example by regression analysis. If a clear trend is found, then the control chart approach is not appropriate, as the fundamental assumption is that conditions are stable. A different approach would be necessary if a temporal trend was present.

5) The control chart may apply to the whole sampling area (e.g., St. Abbs or Bell Rock), or to only part of it (e.g., the central area of the disposal site, or an annulus at some distance from the centre).

6) The control chart may be set up using actual concentrations, or may be set up using transformed (e.g., log transformed) data, if that increases the approximation of the data to normality. It would be possible to set up control chart limits on non-normal data, assuming a degree of skewness, but these would have presentational difficulties (apparent and obvious, greater tolerance of increases in concentration than of decreases).

7) If the control chart is set up on only a limited amount of data, it would be advantageous to include each new set in the set used to establish the chart, provided there was no indication of temporal trend.

8) The control limits could be set up using standard deviations (in the usual way) or using t-distributions. The latter method takes into account the uncertainty in the estimate of the variance of the distribution of the annual means, and results in wider limits. For example, the t-distribution, equivalent to a 2-sigma warning limit, based on five data points, would be approximately 2.8 sigma. A precautionary approach would suggest using the standard deviation only, but bearing in mind the inherent uncertainties in the positions of the warning and action limits.

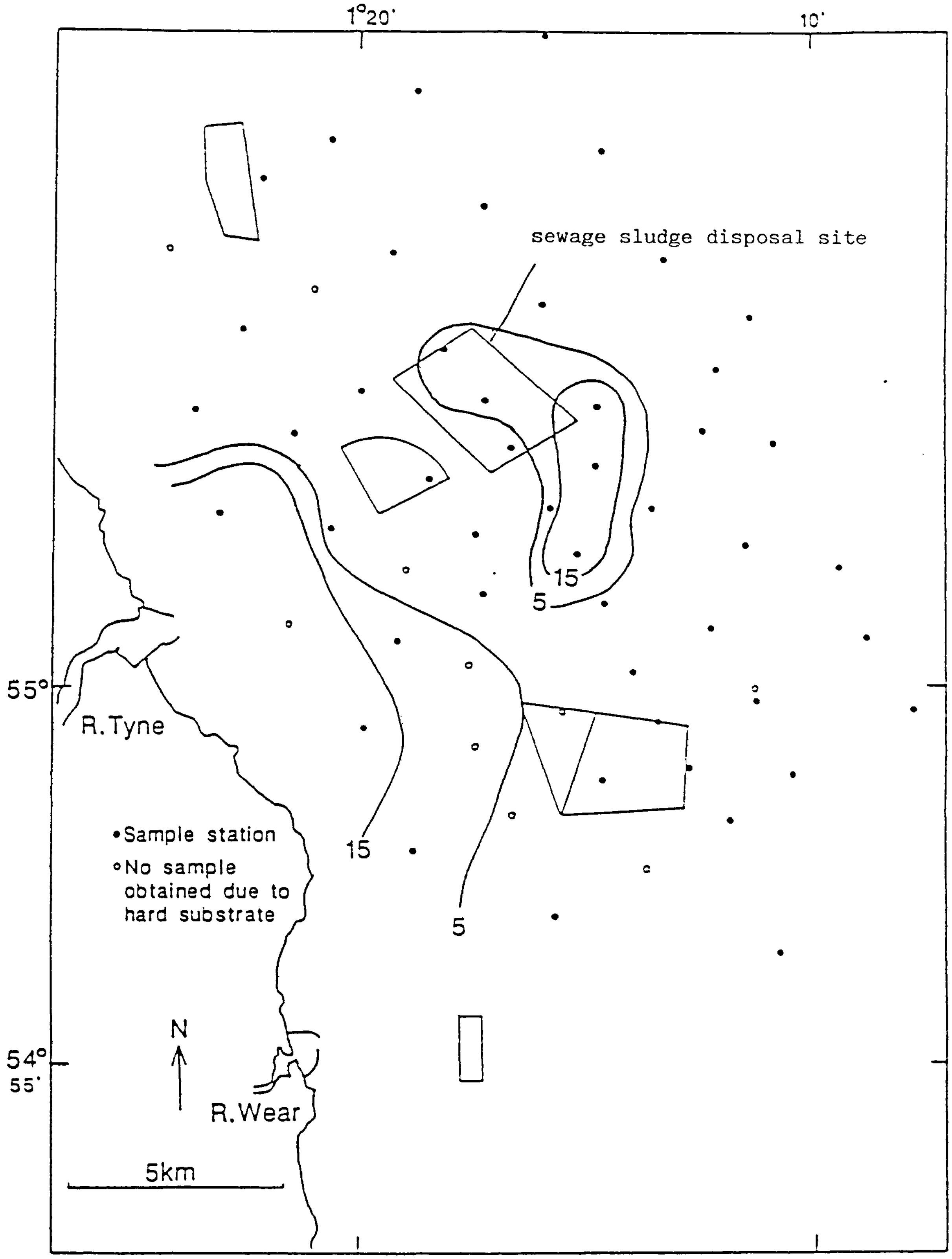


Figure A8.1 Distribution of faecal bacteria in the sediments around the Tyne sewage sludge disposal site, May 1988: *E. coli*.

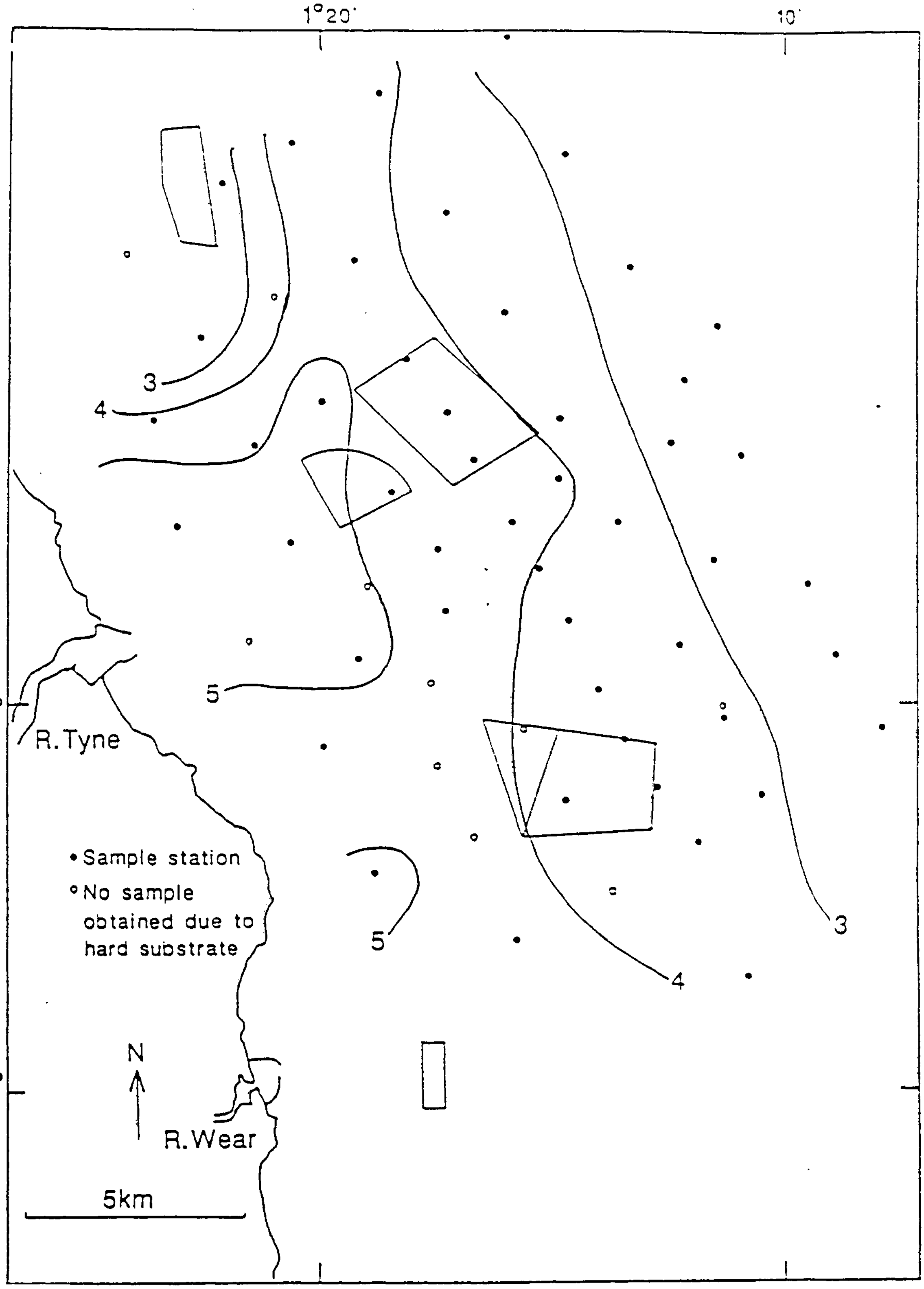
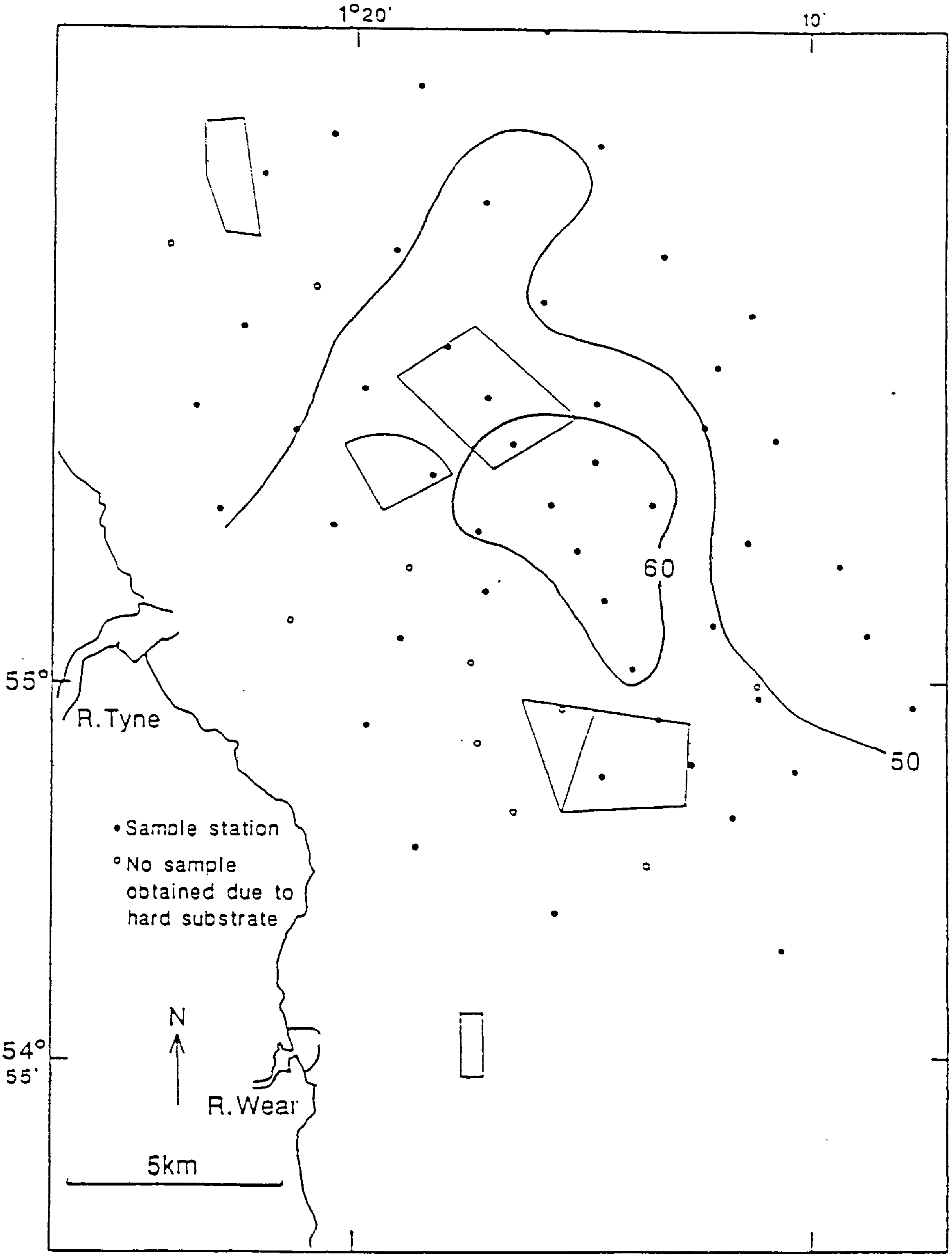


Figure A8.2a Distribution of organic carbon in the sediments around the Tyne sewage sludge disposal site, May 1988.



FigureA8.2b Distribution of metals in the sediments around the Tyne sewage sludge disposal site, May 1988: Chromium.

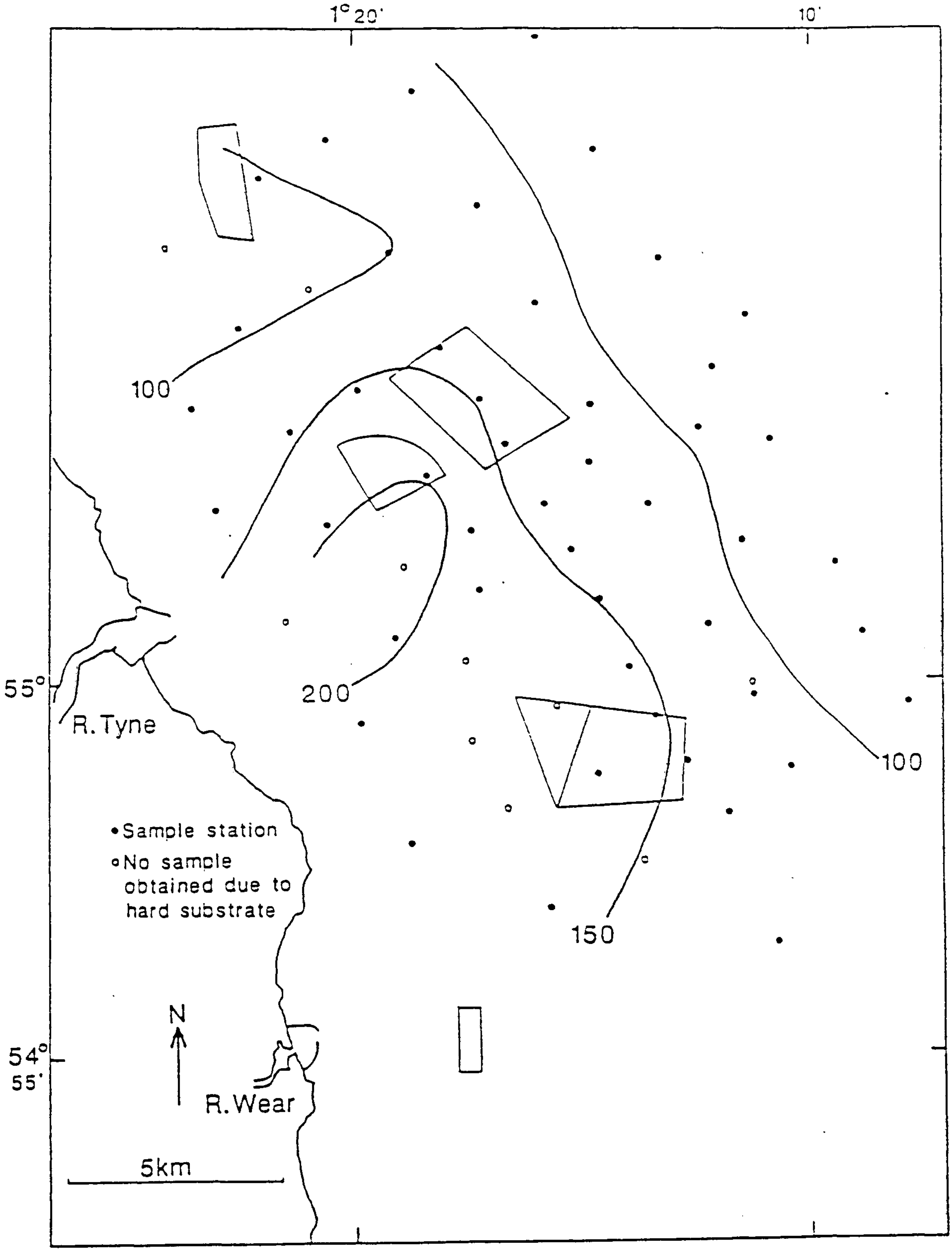


Figure A8.2c Distribution of metals in the sediments around the Tyne sewage sludge disposal site, May 1988: Zinc.

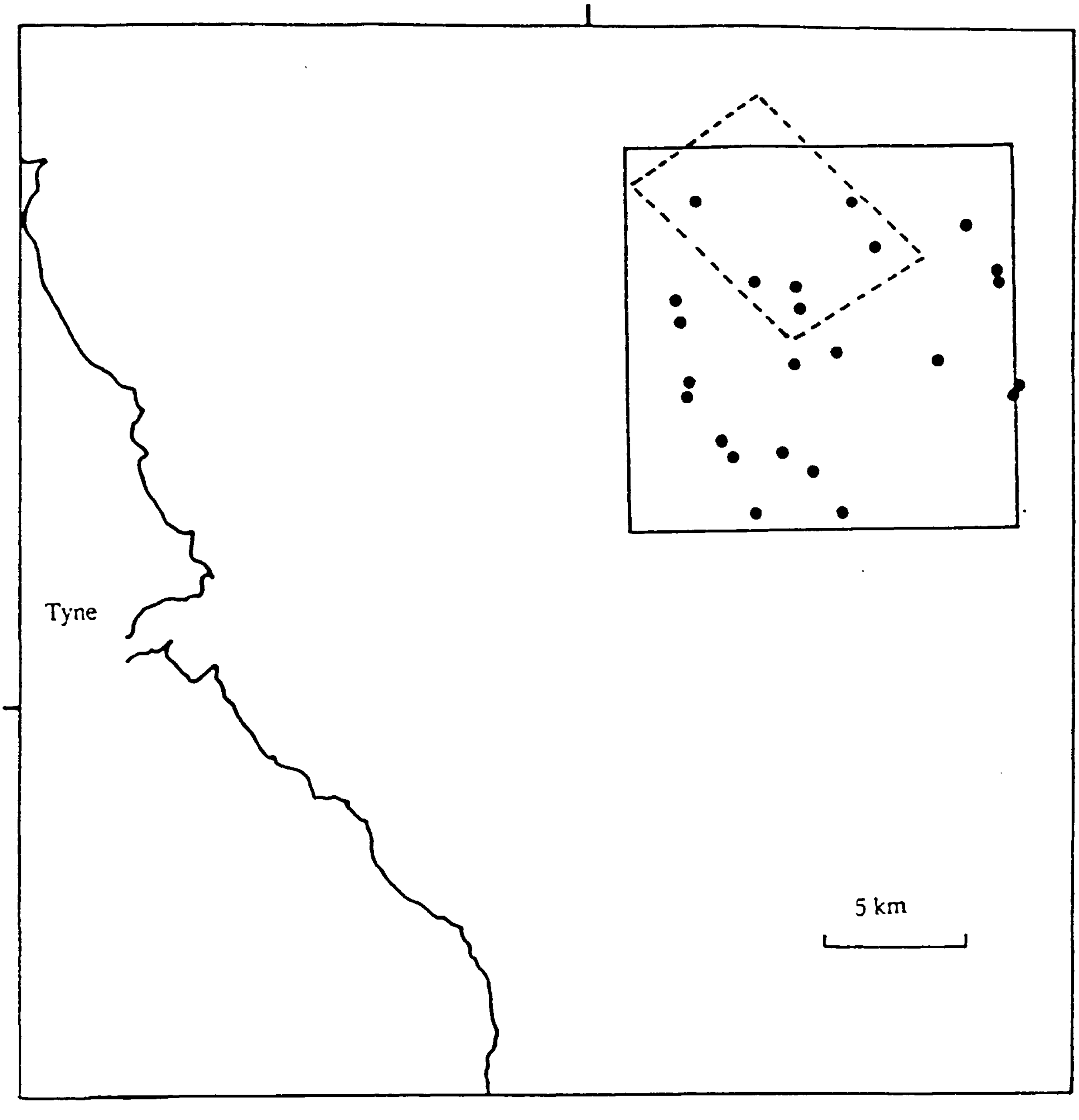


Figure A8.3 Sampling grid used to assess temporal changes in sediment quality off the Tyne.

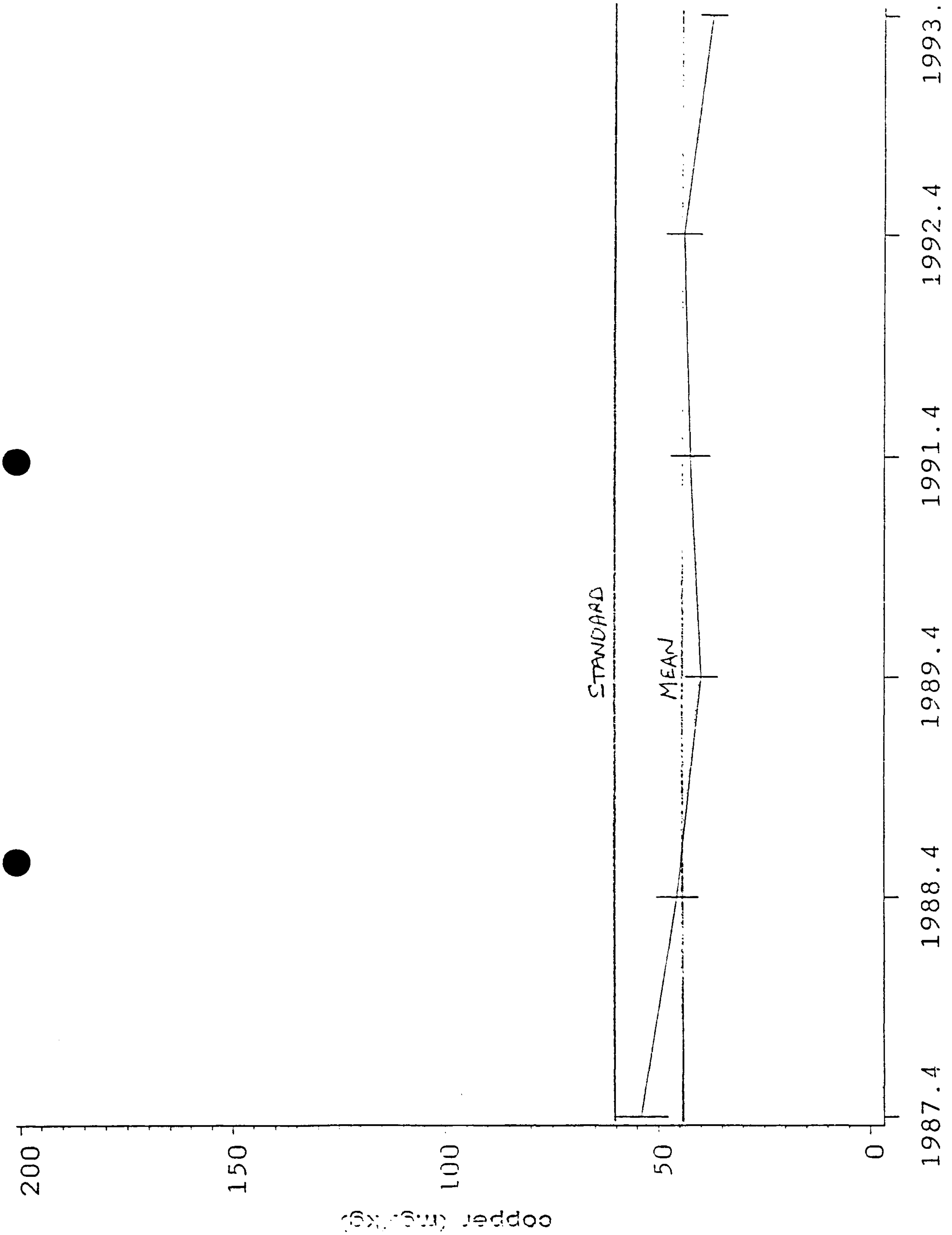


Figure A8.4a Mean concentrations of copper in surface sediments off the Tyne estuary from 1987 to 1993.

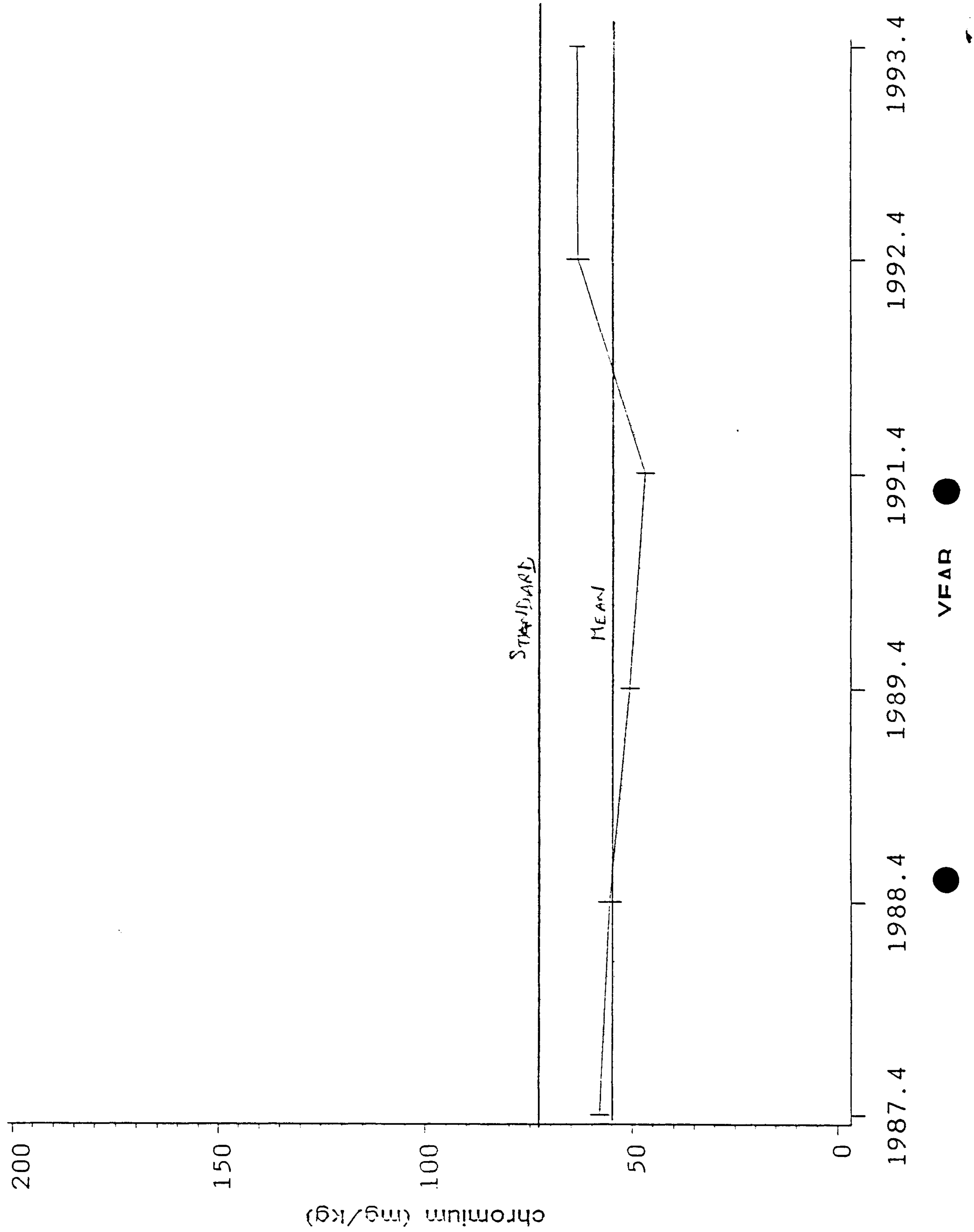


Figure A8.4b Mean concentrations of chromium in surface sediments off the Tyne estuary from 1987 to 1993.

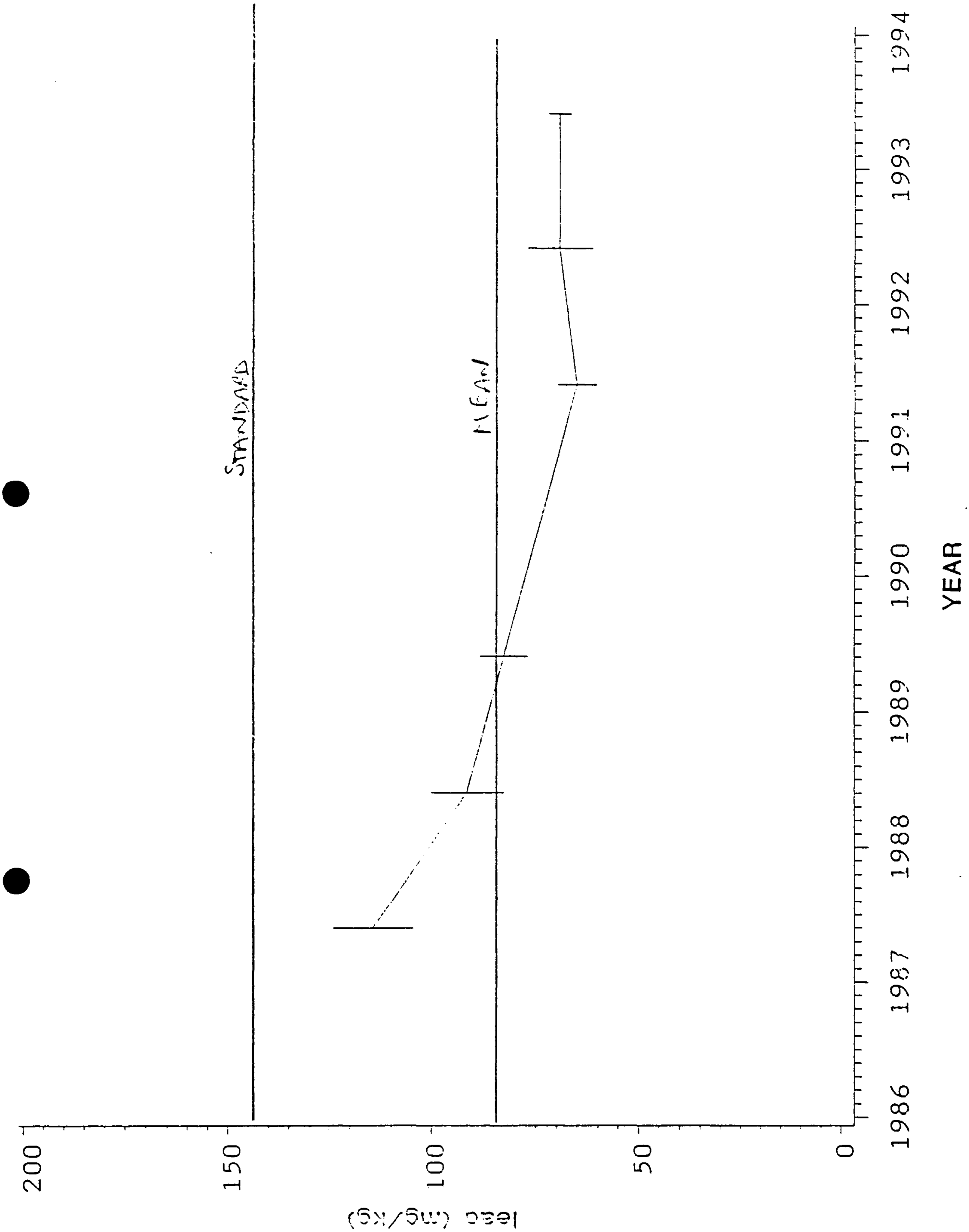


Figure A8.4c Mean concentrations of lead in surface sediments off the Tyne estuary from 1987 to 1993.

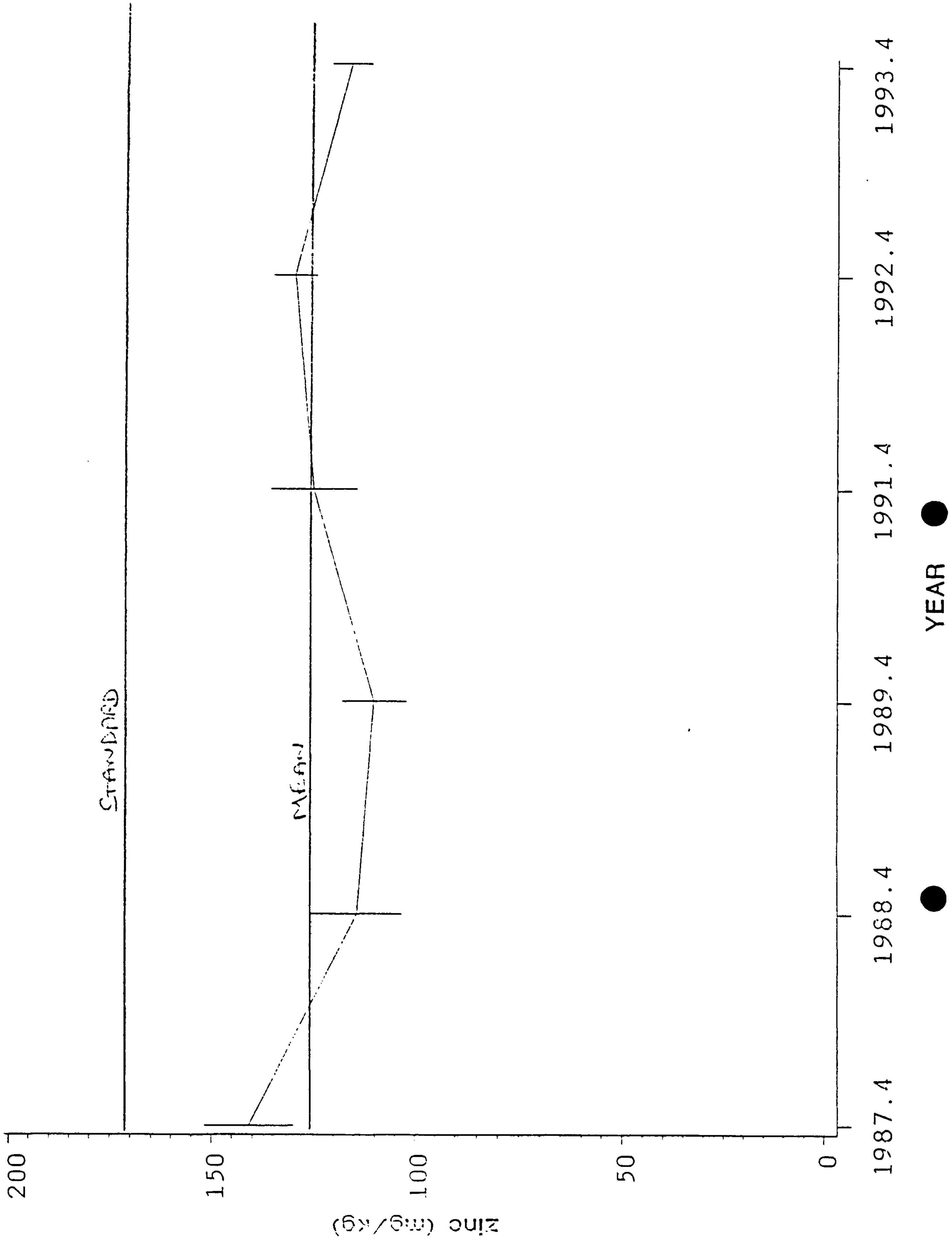


Figure A8.4d Mean concentrations of zinc in surface sediments off the Tyne estuary from 1987 to 1993.

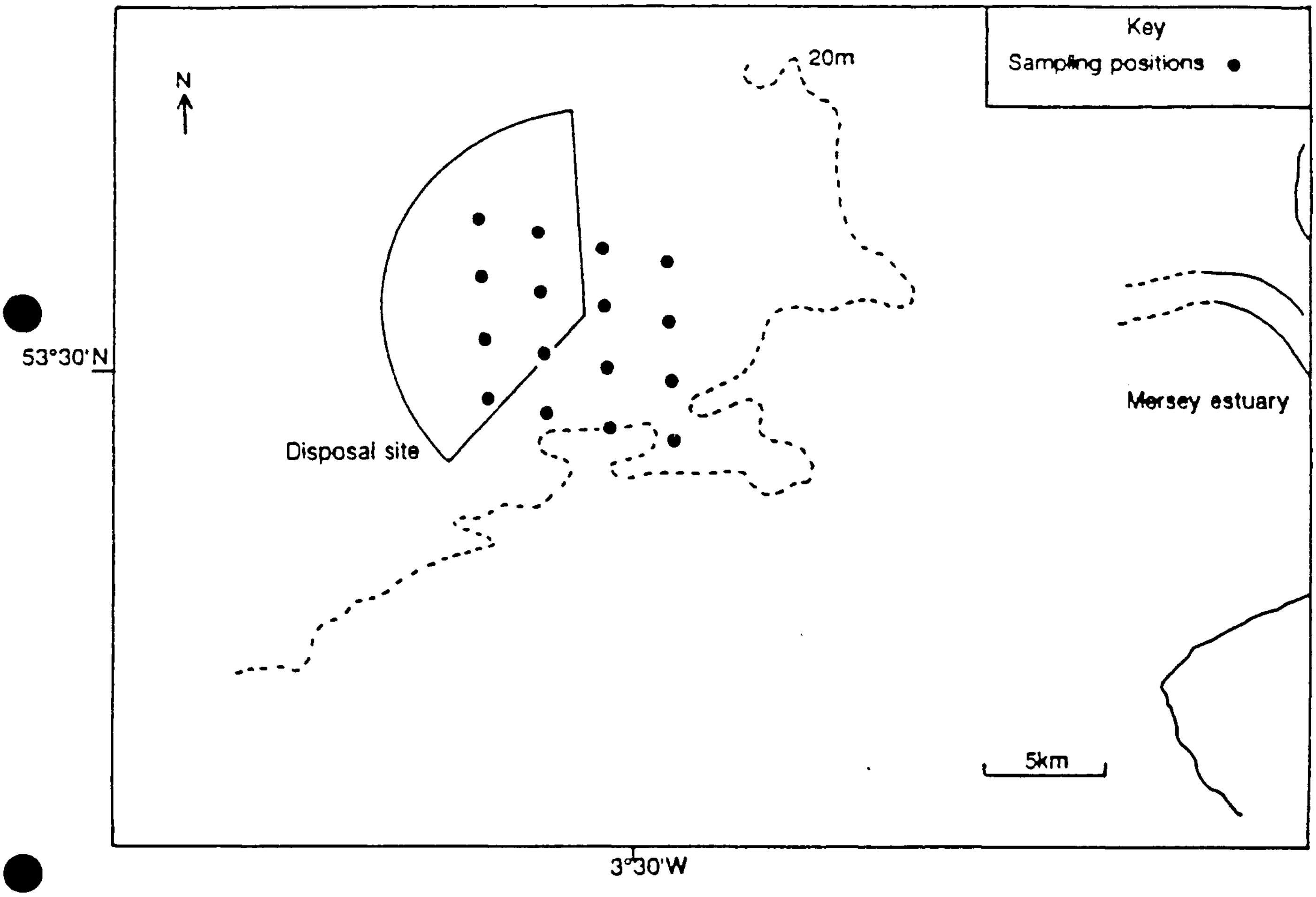


Figure A8.5 The sewage sludge disposal site and sediment sampling grid in Liverpool Bay.

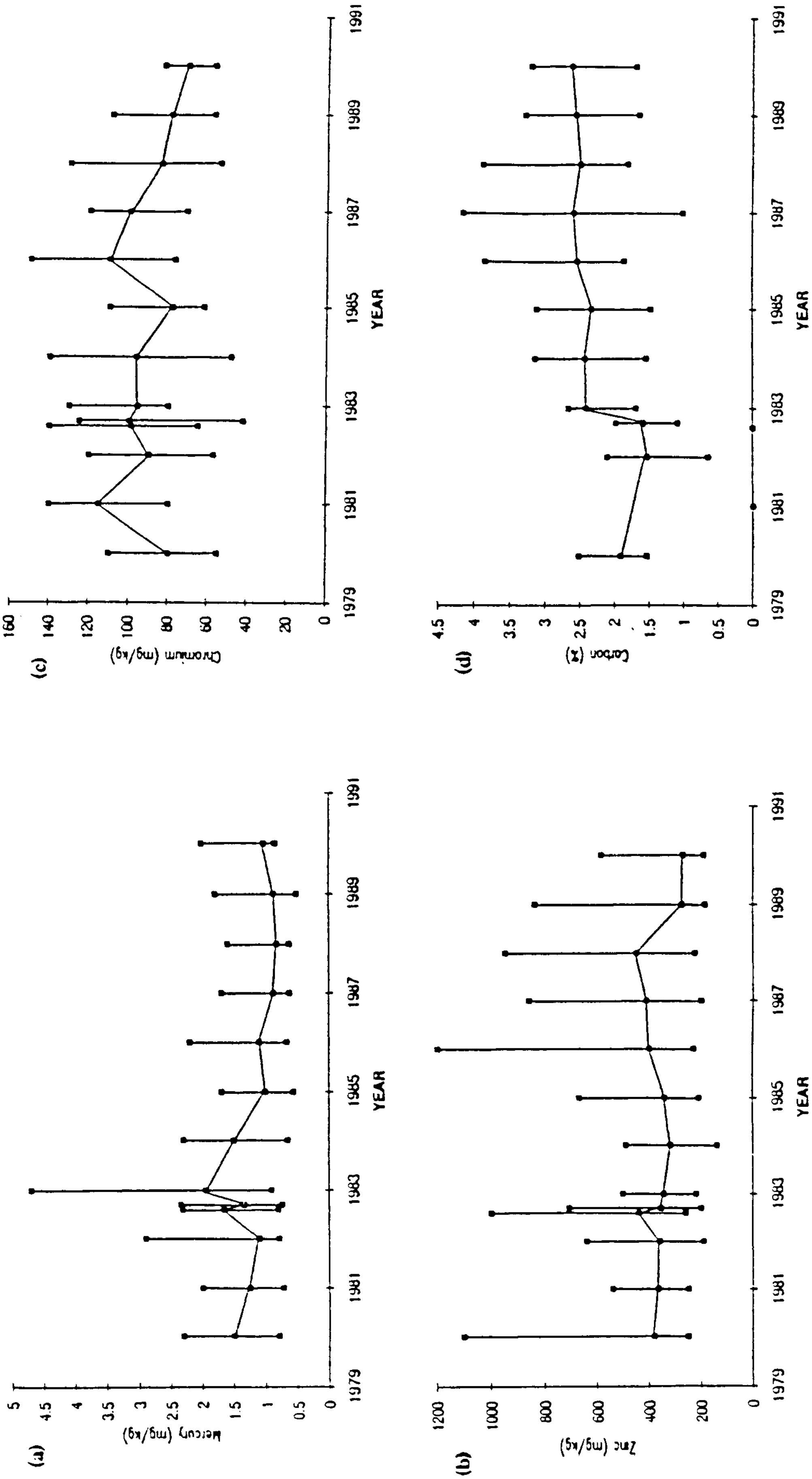


Figure A8.6 Time series of concentrations of carbon and metals in the <90 µm fraction of sediments collected near the Liverpool Bay sewage sludge disposal site: (a) mercury; (b) zinc; (c) chromium; and (d) carbon. Bars show median value and range.

ANNEX 9

SOME DATA ON OFFSHORE TEMPORAL TRENDS IN THE BALTIC SEA

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Expansion of laminated sediments during recent decades

When oxygen conditions close to the bottom are high enough so that benthic animals can live there and mix the sediment, it can be characterized as a homogeneous clay without any visible structures. However, if the oxygen concentrations are low prohibiting benthic fauna from living there, the sediments normally are laminated. The lamination is created by differences in the settling material during different seasons. Since there is no benthic fauna at the bottom the differences in sedimentation will remain and lamina are created almost like an annual ring in a tree. The characteristics of the lamination in the Northern Baltic Proper are summarized in Table A9.1. From studies of cores, it has been concluded that laminated sediments have been deposited naturally for ages in deep parts of the Baltic Proper.

Table A9.1 Characteristics of recently occurring laminated sediments in the offshore areas of the Northwestern Baltic Proper (from Jonsson *et al.*, 1990).

	Mean	S.D	Range	No of cores
Thickness of the laminated layer (cm)	4.5	2.2	0.5–9	21
Number of lamina	19	9	3–40	21
Lamina thickness[1]	2.5	0.8	1.5–4.2	21

[1] average for the upper 5 cm of the laminated layer (mm)

During the late 1940s and early 1950s, reports were published that the benthic fauna were suffering from oxygen deficiency. This is also recorded in the sediments. From counting the number of lamina in cores from the Baltic Proper it has been possible to estimate the expansion of the laminated sediments during recent decades (Figure A9.1). Also in an intensive study offshore area in the NW Baltic Proper (50 km^2; Jonsson *et al.*, manuscript) and in archipelagos (Persson and Jonsson, 1996), similar expansion trends have been found for laminated sediments (Figure A9.1).

In the offshore Baltic Proper, the expansion started in the 1940s. However, the really large eliminations occurred during the 1960s and 1970s. During that period, as an average, a bottom area of approximately 2000 km^2 was extinguished every year. Approximately one third of the bottom area in the Baltic Proper suffers from more or less permanent oxygen deficiency and on the main part of these bottoms, deeper than 75 m, laminated sediments are deposited (Jonsson, 1992).

In the intensive study offshore area, a clear decrease in the laminated area is obvious from the late 1980s and onwards. This has been interpreted as a recolonization by opportunistic benthic fauna of parts of the former laminated sediments due to improved oxygen conditions caused by large inflows of saline water through the Danish Sounds in 1993–1994. The registered time difference is suggested to be caused by bioturbation down to 1–2 cm, corresponding to a time period of some five years.

Increased carbon sequestering

A comparison between sediment data from around 1930 to the late 1980s indicates an almost two-fold increase in organic matter deposition in the northern Baltic Proper during recent decades. From calculations based on annual sequestering of carbon in laminated sediments from the Baltic Proper, carbon originating from primary production and external sources has been estimated to have increased 5 to 10-fold since the turn of the century, and now averages 9 g C m^{-2}yr^{-1} for the period of early 1980 to the late 1980s (Jonsson and Carman, 1994).

This organic matter consumes oxygen when its degraded. The substantially increased supply of carbon to the deep water is presently considered to be the main reason for the bad oxygen conditions in the deep water of the Baltic Proper.

Halogenated compounds in offshore sediment cores

Between the early 1950s and the mid-1980s, the industrial world increased the use of chlorine chemicals ten-fold. A number of these compounds have been found to accumulate in biota and sediments. However, despite this, we still lack investigations on many new chemicals. With a few exceptions, we only have information on the traditional ones, e.g., PCBs, DDTs and PCDD/Fs.

Since there are several factors that may influence the record in sediment core profiles (e.g., degradation, lipid pool changes, water solubility, changed redox conditions), conclusions from retrospective sediment studies of halogenated compounds must be drawn with great care.

Sediment profiles of different types of chlorinated compounds show in general quite similar concentration profiles in sediment cores, characterized by substantially increased concentrations from the 1950s and onwards; in some of the cores (especially NW Baltic Proper) thereafter somewhat decreasing after the 1970s and 1980s, in most of them further increasing (e.g., Perttilä and Haahti, 1986; Jonsson, 1992; deWit *et al.*, 1990; Nylund *et al.*, 1992; Axelman *et al.*, 1995; Witt, 1995; Kjeller and Rappe, 1995). In the Baltic Proper, rapidly increased concentrations coincide with the change from bioturbated to laminated sediments. This turnover seems to have led to substantially increased concentrations of several different contaminants and may therefore not reflect the anthropogenic load to the Baltic.

Most interesting, however, is the increasing concentrations of PCBs during recent decades. This is exemplified by a profile from the Eastern Gotland Deep (see Figure A9.2), sampled during the Baltic Sea Sediment Baseline Study 1993. By means of 137Cs, 8 cm has been suggested to represent 1986, indicating a deposition rate of more than 1 cm uncompacted sediment per year in this area. PAHs (sum of 18 compounds) describe a distribution profile similar to that of Cd, showing a submaximum around 1980, thereafter decreasing substantially. PCBs (sum of 7 congeners), however, show a quite different distribution with gradually increasing concentrations during recent decades, indicating an increased load of PCBs to the Baltic Proper. This is contradictory to the decreasing PCB concentrations in biota, which are indicating a decreasing PCB load.

The PCDD/Fs concentrations were found to be 10–30 times higher in surficial (0–1 cm) than in deep (20–35 cm) sediments (Jonsson *et al.*, 1993; Kjeller and Rappe, 1995). The isomeric patterns differed significantly between the surficial and the deep sediments which excluded contamination of the 100–400 year-old deep layers, indicating a natural production of PCDD/Fs. Also for the PCDD/Fs rapid concentration increases were found when the sediments changed from bioturbated to laminated.

In a sediment core from the Bornholm Deep (Nylund *et al.*, 1992), polybrominated diphenyl ethers (PBDE) show a more rapid increase towards the sediment surface than for sPCB and sDDT (Figure A9.3). This may be an indication of a recent substantially increased use of PBDE as flame retardants, but may also be an indication of different degradation rates and/or water solubility. However, this may serve as an example that sediment studies are valuable tools to identify future problems related to halogenated compounds.

Conclusions

Substantial temporal changes in the area of laminated sediments have been registered in offshore areas and archipelagos in the Baltic Proper. Temporal trends in areas of laminated sediments may serve as a good monitoring parameter since it integrates the eutrophication situation. Sequestering of carbon, deriving from primary production and external sources, has increased 5–10-fold in the Baltic Proper since the turn of the century.

The turnover from bioturbated to laminated sediments seems to have led to substantially increased concentrations of several different contaminants and may therefore not reflect changes in the anthropogenic load to the Baltic.

PCB concentrations increased gradually in laminated sediments in the Baltic Proper during recent decades, indicating an increased load of PCBs; PCB concentrations have decreased substantially in biota since the 1970s, indicating a decreasing PCB load.

References

de Wit, C., Jansson, B., Strandell, M., Jonsson, P., Bergqvist, P.-A., Bergek, S., Kjeller, L.-O., Rappe, C., Olsson, M. and Slorach, S., 1990. Results from the first year of the Swedish dioxin survey. Chemosphere, 20:1473-1480.

Jonsson, P., Carman, R. and Wulff, F., 1990. Laminated sediments in the Baltic - A tool for evaluating nutrient mass balances. Ambio, 19 (3): p: 152–158.

Jonsson, P., 1992. Large-scale Changes of Contaminants in Baltic Sea sediments during the Twentieth Century. Doctoral thesis at Uppsala University. ISBN 91-554-2997-1.

Jonsson, P., Carman, R., Jonsson, J. and Sivertsson, K. Bottom dynamics in the NW Baltic proper (manuscript).

Jonsson, P., Rappe, C., Kjeller, L.-O., Kierkegaard, A., Häkanson, L. and Jonsson, B., 1993. Pulp mill related polychlorinated organic compounds in Baltic Sea sediments. Ambio 22:37–43.

Jonsson, P. and Carman, R., 1994. Changes in sediment deposition of organic matter and nutrients in the Baltic Sea during the twentieth century. Marine Pollution Bulletin 28:417–426.

Kjeller, L.-O. and Rappe, C., 1995. Time trends in levels, patterns and profiles for polychlorinated dibenzodioxins, dibenzofurans, and biphenyls in a sediment core from the Baltic proper. Environmental Science and Technology, 29:346–355.

Nylund, K., Asplund, L., Jansson, B., Jonsson, P., Litzon, K. and Sellstrom, U., 1992. Analysis of some polyhalogenated organic pollutants in sediment and sewage sludge. Chemosphere 24:1721–1730.

Persson, J. and Jonsson, P. Eutrophication-induced changes of bottom conditions in a Swedish archipelago (manuscript).

Perttilä, M. and Haahti, H., 1986. Chlorinated hydrocarbons in the water and sediments of the seas around Finland Publications of the Water Research Institute, National Board of Waters, Finland, No. 68:197–200.

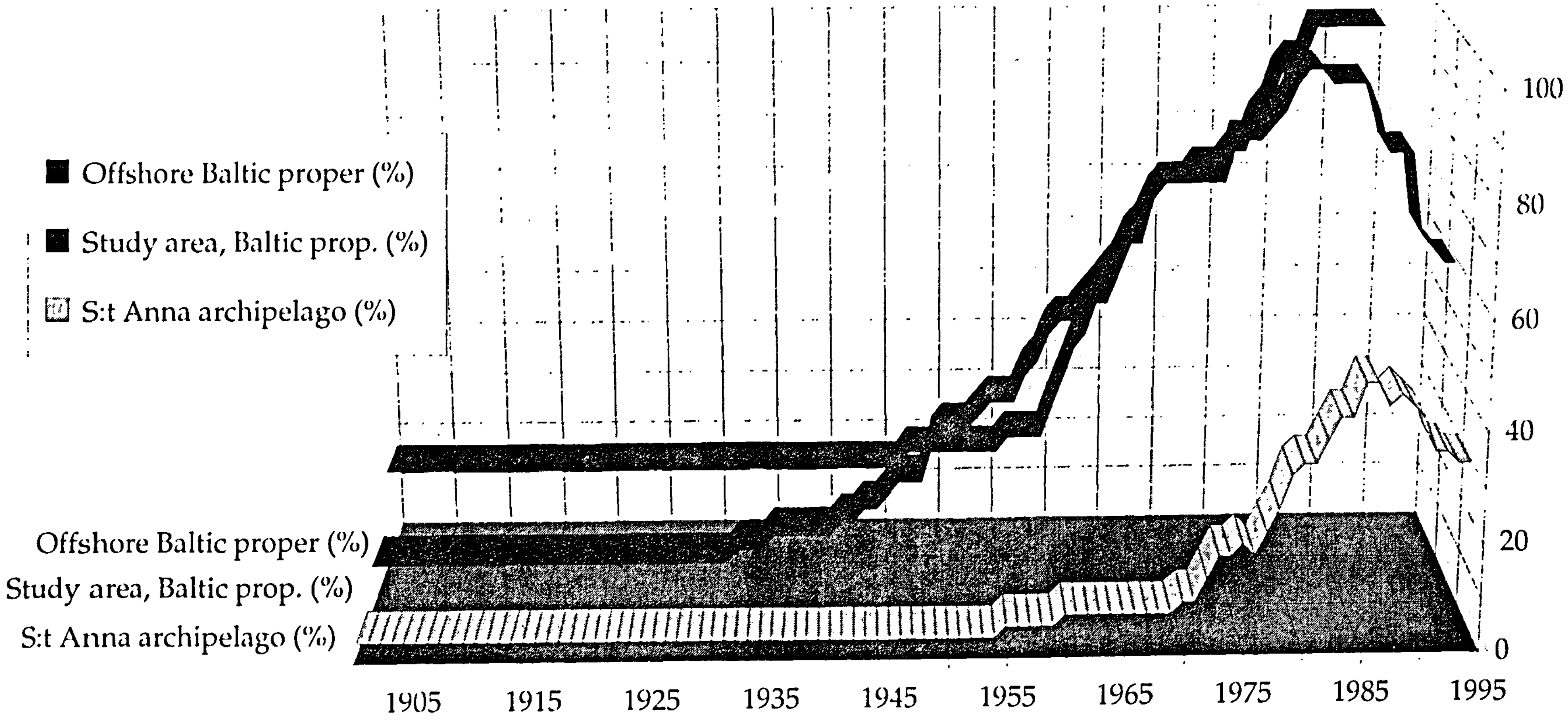

Figure A9.1 Estimated temporal variations of the extension of laminated surficial sediments in the offshore Baltic Proper, an intensive study in the NW Baltic Proper and S:t Anna archipelago, Sweden. (From Jonsson *et al.*, 1990).

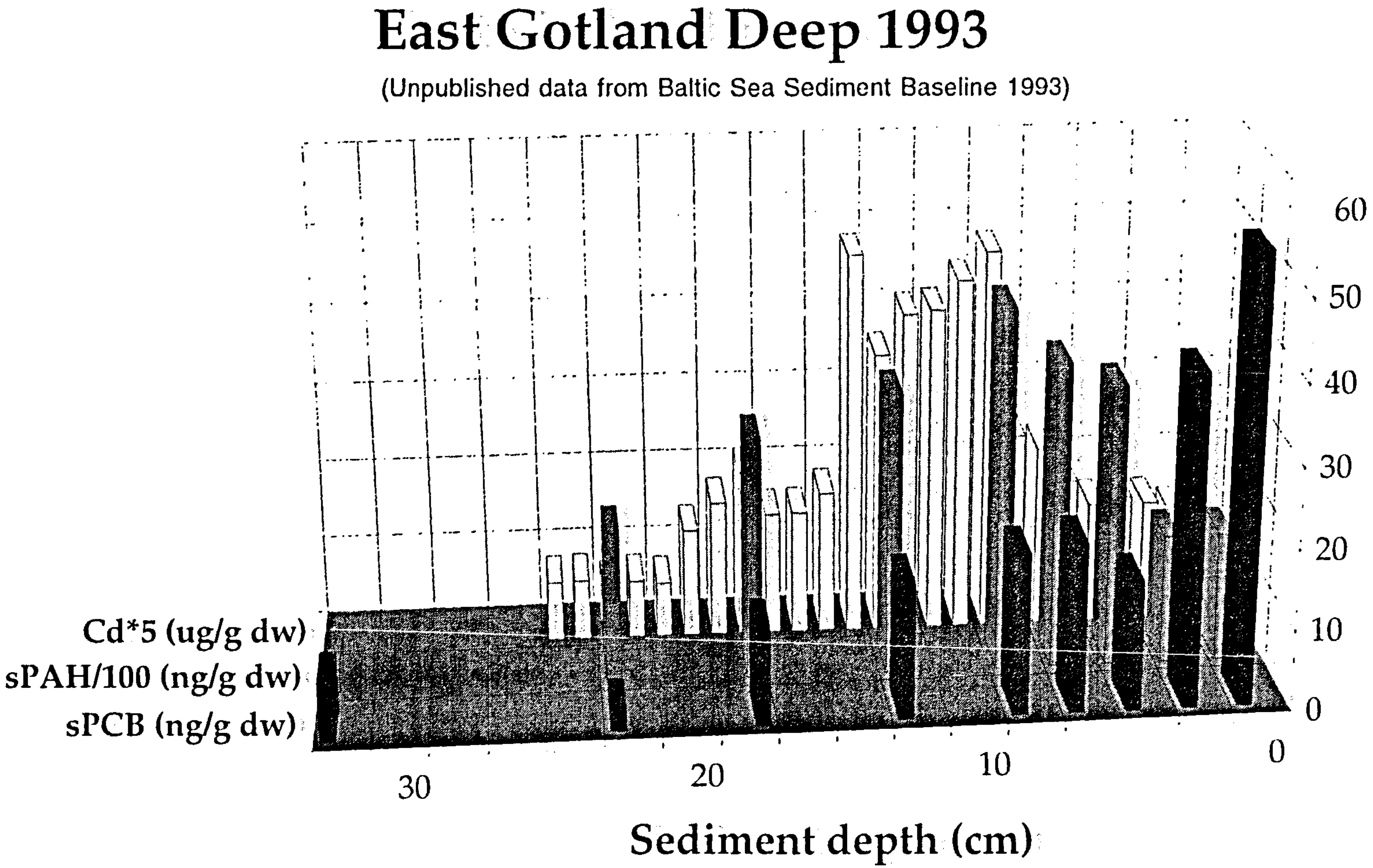

Figure A9.2 Concentrations of PCBs (sum of 7 congeners), PAHs (sum of 18 compounds) and Cd in a profile from the East Gotland Deep, sampled during the Baltic Sea Sediment Baseline Study 1993.

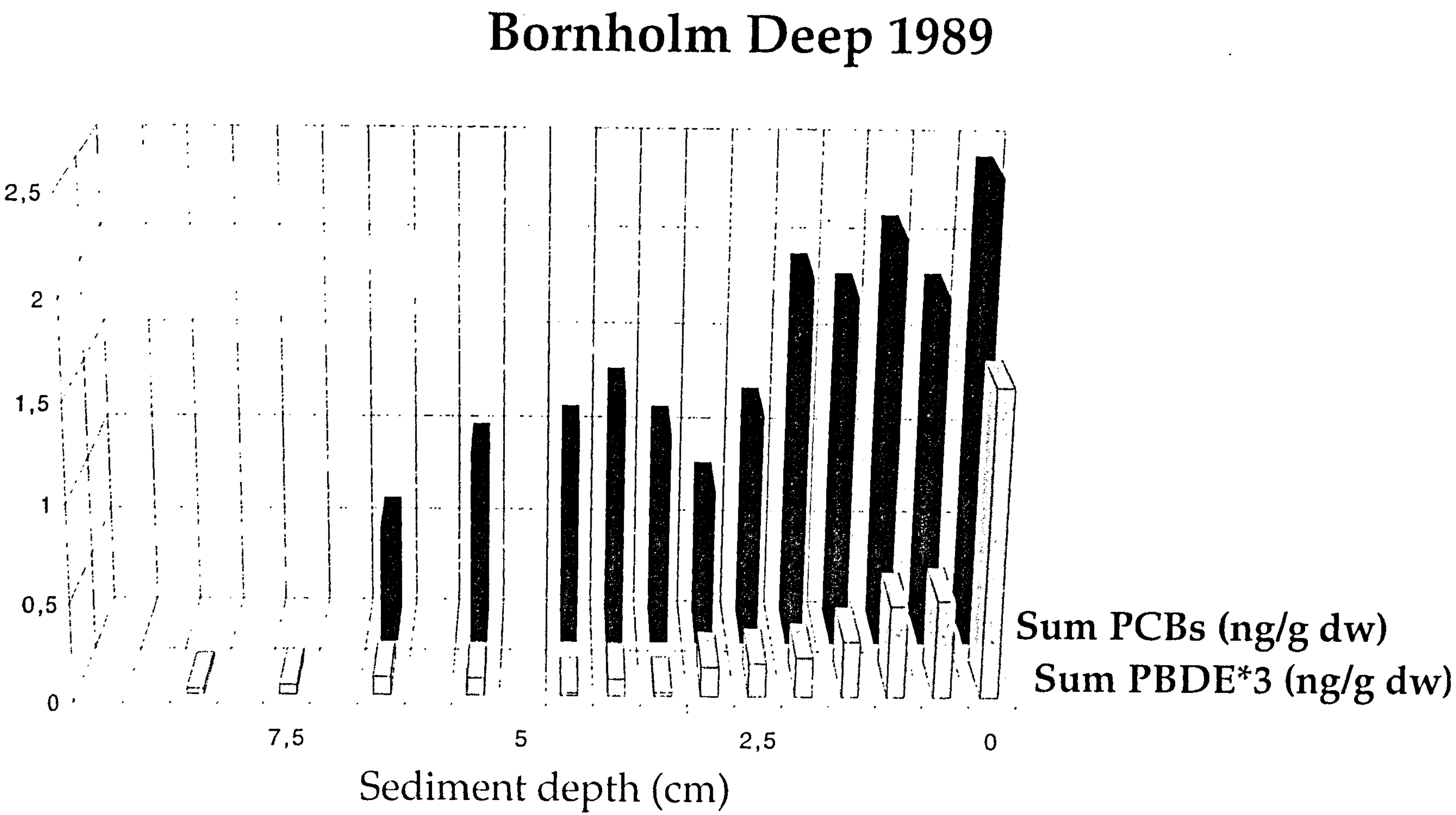

Figure A9.3 Sum PCBs (4 congeners) and sum PBDE (3 congeners) in a naturally laminated sediment core from the Bornholm Deep, Southern Baltic Proper (From Nylund *et al.*, 1992).

ANNEX 10

DEGRADABILITY OF EXTRACTABLE ORGANIC CHLORINE (EOCl)

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EOCl - a pulp mill tracer

EOCl (extractable organic chlorine) is a sum parameter that has proven useful when it comes to trace large-scale distribution of discharges of chlorinated compounds from pulp mill bleacheries. In EOCl most of the well-known substances like DDTs, PCBs, toxaphenes, chlorophenols and dioxins are included. Only a minor part (<10%) of the EOCl in sediments, however, has been identified (Södergren, 1993). EOCl is important from an ecotoxicological point of view, since it includes the potentially bioaccumulated substances.

By analysing EOCl in surficial sediments in the Baltic Sea, the large-scale distribution of chlorinated compounds from pulp mills becomes obvious (Figure A10.1) with very high EOCl concentrations close to the mills (Jonsson, 1992).

Besides the distribution pattern of EOCl, analyses of specific substances have clearly identified bleachery effluents as large sources of chlorinated compounds to the Baltic Sea. Gradient studies off the Iggesund mill in the Bothnian Sea (Jonsson *et al.*, 1993) strongly indicate that the mill is the source of a number of PCDD/F congeners (2,3,7,8-TCDD, 2,3,7,8-TCDF, 1,2,7,8-TCDF, 1,2,3,7.8-PnCDD), alkyl-CDFs, 3,4,5-TCG and TeCG. The appearance in the central parts of the Baltic of 3,4,5-TCG, which so far only has been related to pulp mills (Grimvall *et al.*, 1991), also indicates the large-scale influence of pulp mills. High correlations have been obtained between EOCl and these substances, supporting the conclusion that EOCl is a useful parameter for tracing pulp mill discharges in surficial sediments.

Furthermore, the only known source of alkyl-CDFs is pulp mill discharges. Thus, the identification of alkyl-CDFs not only in the Iggesund gradient, but also in the central parts of the Bothnian Sea and the northern, Baltic Proper (Kjeller and Rappe, 1995) support the conclusion on a large-scale distribution of 'pulp mill' compounds in the Baltic.

Degradability

EOCl mass balance

To check the large-scale influence of pulp mill discharges, a mass balance study was carried out on EOCl, based on direct measurements and historical emission data from the pulp mills (see Figure A10.2) (Wulff *et al.*, 1993). Measurements were carried out during 1988 and 1989 in river runoff, precipitation, sea water and sediments to estimate the input/output and to calculate the stores in water and sediments.

The discharges from pulp mills clearly dominated the input (75%), while the input via rivers is negligible (<2%). The atmospheric input has been calculated to be 23% of the total (Figure A10.2). More than 50% of the input since the early 1940s is still stored in the Baltic system, although a substantial part must have left the Baltic through the Danish Straits. The main part (80%) of the store is found in the sediments and the rest in the water mass.

Since the main input goes into the Bothnian Sea, where the coastal sediments show remarkably high concentrations (cf. Figure A10.1), one might expect to find most of the EOCl stored in the coastal sediments. However, estimates yield that, despite the high concentrations close to the mills, these coastal sediments contain only some 10% of the total sediment store. About 90% is dispersed from the discharges into the open sea areas, and the main part (ca. 60%) of the sediment store is found in the sediments of the Baltic Proper, indicating a large-scale transport of EOCl. Independent checks of the annual input of EOCl to the sediments from the large material of EOCl in surficial sediments are in agreement with these results.

One important conclusion to be drawn from the mass balance study is that a major part of the total input of EOCl since the 1940s is still stored in the Baltic sediments, indicating a substantial persistence and resistance to degradation.

Degradation experiment

A two-year incubation study of pulp mill contaminated sediments (Granmo *et al.*, 1991) in various environments (Figure A10.3; aerobic, anaerobic, sediment suspension, flow-through and closed systems, different temperatures) indicated a degradation half-time of EOCl in decades rather than months/years, supporting the results of the mass balance study. Only under flow-through conditions could a significant decrease be detected. However, rather than being considered as an indication of degradation, this loss was interpreted as a removal via the through-flowing water.

Persistence to sulphuric acid

A substantial part (mean 10–15%) of EOCl is persistent to treatment with concentrated sulphuric acid (e.g., Östfeldt *et al.*, 1994; Gustavson and Jonsson, manuscript), which is another criteria for environmental hazards. In a sediment data set from the Baltic Sea, the Kattegat and the Skagerrak, collected within a joint Nordic project, EOCl is correlated to EPOCl (r=0.80). The concentration of EOCl is in the range 0.1–6.2 mg/g dw, and as a mean, 11.4% is in the sulphuric acid resistant fraction EPOCl. Håkanson *et al.* (1988) investigated EOCl concentrations in relation to EPOCl in coastal areas of the Bothnian Sea. Although the range in concentrations is quite different (11–900 mg/g dm), the same proportion of EOCl is persistent (11.9%). If these two sets of data are combined on a logarithmic scale, a strong linear relationship appears (Figure A10.4). Because of the degradation process, one should expect to find a higher proportion of the persistent fraction far away from discharge sources. Following Jonsson *et al.* (1993) and Wulff *et al.* (1993), who considered the Bothnian Sea to be the area most polluted from pulp mills, we expected to find a relatively lower proportion of the EPOCl in this area, and an increasing proportion approaching the Atlantic Ocean. Surprisingly, however, the relation was quite constant at all the stations, with the EOCl concentration interval ranging from 0.1–900 mg/g dm. The same ratio (ca. 12%) was also found in mussels from the Baltic. One possible explanation might be that not only EPOCl, but also EOCl is quite persistent in the aquatic environment.

Conclusions

The results from an EOCl mass balance study suggest that a major part of the total input of EOCl since the 1940s is still stored in the Baltic sediments, indicating a substantial persistence and resistance to degradation for EOCl.

A two-year incubation study of pulp mill contaminated sediments indicated a degradation half-time of EOCl in decades rather than months/years.

A substantial part (10–15%) of EOCl is resistant to treatment with concentrated sulphuric acid.

References

Granmo, Å., Jonsson, P., Brydsten, L., Ekelund, R., Magnusson, K. and Berggren, M., 1991. Long-term degradation test with coastal Baltic Sea sediments contaminated with extractable organic halogens. In: Södergren, A. (Ed.) Environmental fate and effects of bleached pulp mill effluents. Proceedings of a SEPA Conference held at Grand Hotel Saltsjöbaden, Stockholm, Sweden, 19-21 November 1991. SEPA Report 4031, ISBN 91-620-4031-6, pp. 68-73.

Grimvall, A., Stålnacke, P., Sundblad, K., Niemirycz, E., Pitkänen, H., Bruhn, A., 1991. Trend analysis of nutrient concentrations in Baltic Sea rivers. In: Environment, Energy and Natural Resource Management in the Baltic Region. Proc. 3rd Int. Conf. on System Analysis. Fenger, J., Halsnaes, K, Larsen, H., Schroll, H. and Vidal, V. (eds). Nord 1991:48, Copenhagen.

Gustavson, K. and Jonsson, P. Halogenated organic compounds in mussels and sediments along a transect from the Bay of Bothnia to the Atlantic (Manuscript).

Håkanson, L., Jonsson, B., Jonsson, P. and Martinsen, K., 1988. Påverkansområden för klorerat organiskt material från massablekerier. SNV Rapport 3522. 165 s, English summary 12 pp.

Jonsson, P. 1992. Large-scale changes of contaminants in Baltic Sea sediments during the twentieth century. Doctoral thesis at Uppsala university. ISBN 91-0-554-2997-1.

Jonsson, B. 1993. Pulp mill related polychlorinated organic compounds in Baltic Sea sediments. Ambio 22:37–43.

Kjeller, L.-O. and Rappe, C., 1995. Time trends in levels, patterns and profiles for polychlorinated dibenzo-*p*-dioxins, dibenzofurans, and biphenyls in a sediment core from the Baltic proper. Environmental Science and Technology, 29:346–355.

Södergren, A., Adolfsson-Erici, M., Bengtsson, B.-E., Jonsson, P., Lagergren, S., Rahm, L. and Wulff, F., 1993. Bleached Pulp Mill Effluents - Fate and Effects in the Baltic Sea. Swedish Environmental Protection Agency Report 4047, 150 pp.

Wulff, F., Rahm, L., Jonsson, P., Brydsten, L., Ahl, R. and Granmo, Å. 1993. A mass balance of chlorinated organic matter for the Baltic Sea - A challenge to ecotoxicology. Ambio 22:27–31.

Østfeldt, P., Gustavson, K., Jansson, B., Jonsson, P., Miettinen, V., Ringstad, O. and Wesén, C., 1994. Halogenated Organic Compounds in the Marine Environment 1989-1990. TemaNord 1994:591 ISBN 92 9120 517 6, 130 pp.

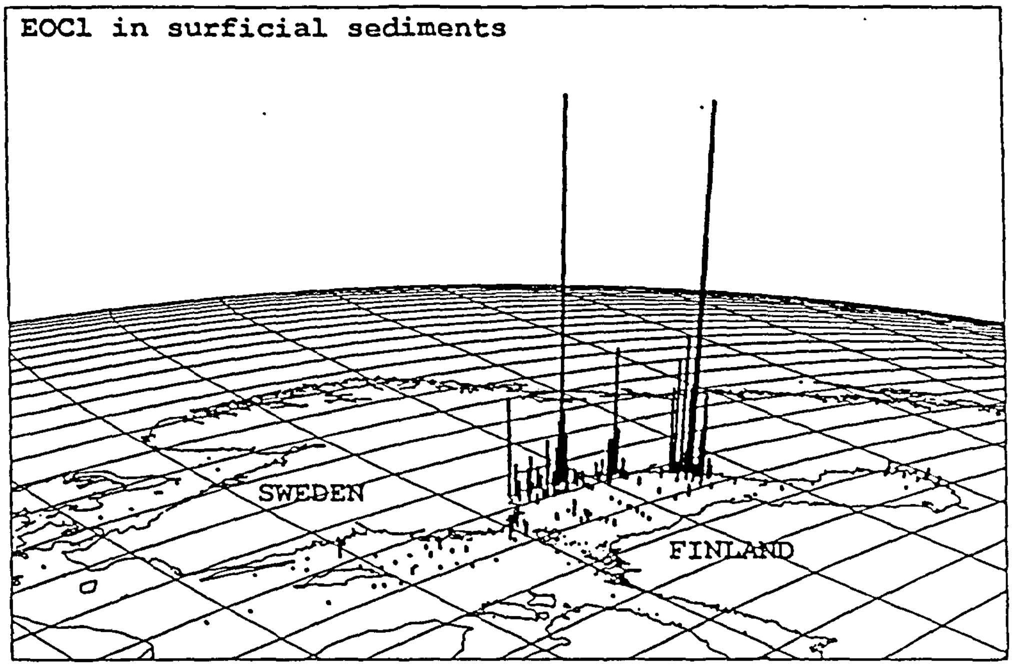

Figure A10.1 Levels of extractable organic chlorine (EOCl) in sediment of the Baltic Sea during 1986–1990 (From Jonsson, 1992).

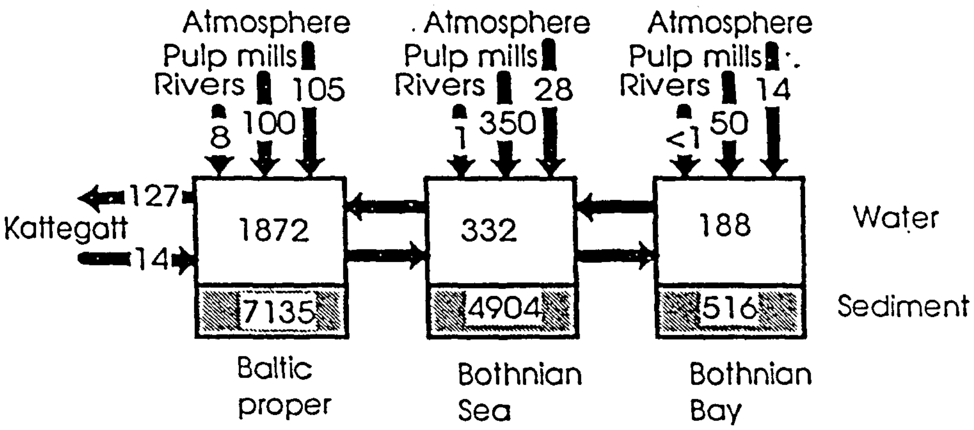

Figure A10.2 A mass balance for EOCl for the three sub-basins of the Baltic Sea based on data from 1988–1989. Input data are given in t/yr and the stores in sediment and water mass in tonnes. (From Wulff *et al.*, 1993).

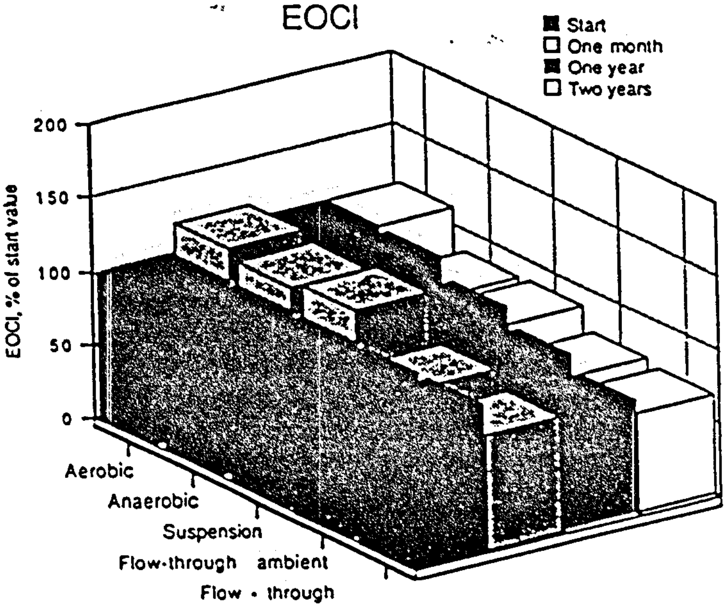

Figure A10.3 A two-year degradation experiment with EOCl in sediments from a pulp mill recipient in the Bothnian Sea. (From Granmo *et al.*, 1991).

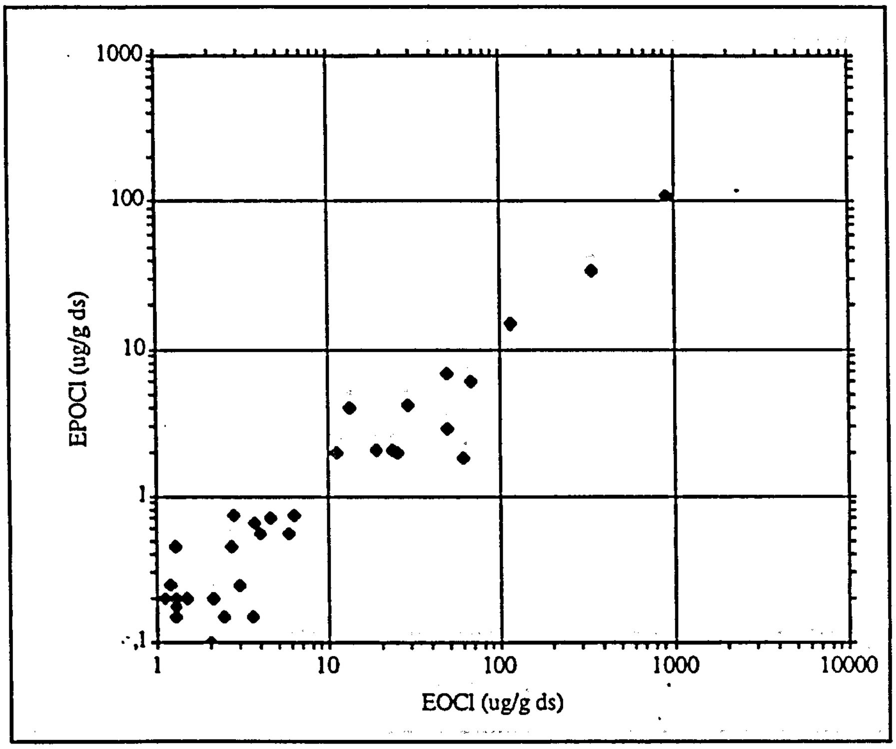

Figure A10.4 EOCl plotted versus EPOCl in sediments from the Baltic Sea, the Kattegat and the Skagerrak. (From Gustavson and Jonsson, ms).

ANNEX 11

SAMPLING VARIABILITY

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Differences between analytical results for multiple samples can be a result of:

(1) contamination during sample processing, from containers, sieving or freeze drying

Handling after sampling can give rise to contamination as the transfer of a sediment sample from a relatively clean offshore area to a more inland area for analysis, where the pollution level is usually higher, will automatically mean that it will tend to take up contaminants from the air. This can occur during storage, sieving or freeze drying.

(2) analytical variability in the contaminant or normalizer concentrations

Analytical variation is inevitably included in sampling variability and will set a lower limit to the attainable sampling variability.

(3) physical inhomogeneity of the sampling area

Variation arises as a result of inhomogeneous grain size distribution. This can be corrected for by normalization techniques, although it must be recognized that the result is then subject to additional analytical error. Samples are never homogeneous at every scale. If the sample intake to the analytical procedure is low, there is a larger chance of deviating results between subsamples. Further, by sieving, a sample is obtained which is very inhomogeneous due to the sieving process, but even more so following the centrifugation step. Incomplete homogenization contributes to the sampling variability.

(4) chemical inhomogeneity of the sampling area

When the sampling area is not homogeneously polluted, the difference between samples will apparently be very high, but in fact the spatial variation is being measured. In such cases it is not realistic to add this patchiness to the sampling variability.

(5) variation in the depth of sampling

In low energy environments where steady sedimentation produces layers with different pollution levels, a variation in the sampling depth will also contribute to the sampling variation. A grab sampler does not normally allow adequate control of sampling depth.

(6) other factors.

In the following discussion, items 4 and 5 are, by definition, not included in the sampling variability as they are considered to be the targets of measurement. If patchiness (4) is present, an adequate sampling strategy has to be chosen to achieve the desired result.

Data and methods

The data used for studying sampling variation are from the sediment monitoring programme of the Netherlands for the years 1990 and 1993. The areas involved are the Ems-Dollard, Wadden Sea, North Sea (nearshore and offshore) and Western Scheldt. At each location, six samples were taken at a distance from each other equal to or larger than the year-to-year precision of the position. In fact, the samples were taken in an area of approximately 100x100 m. On tidal flats, samples were collected manually. From ships, a boxcorer was used. Randomly, pairs of samples were pooled to give three samples for further processing. In addition, 15 samples were taken on the Oyster Grounds for studying the sampling variability, while at two locations van Veen grab samples were also taken close to the boxcore samples.

All samples were sieved at 63 µm with water from the location or with water of the appropriate salinity prepared from offshore sea water by mixing with milli-Q. After sieving, the samples were freeze-dried and homogenized using a ball mill. Heavy metal analyses were done by GFAAS, FAAS or ICP-AES after digestion with concentrated nitric acid in a Teflon bomb at 140 °C for 16 hours. Elemental organic carbon was analysed with a Carlo Erba elemental analyser after carbonates had been removed by exposing the sample to HCl vapour for 24 hours. The sample for CBs was extracted in a hot Soxhlet for 4 hours with 25% acetone in hexane (after addition of recovery standards). After clean-up and addition of an internal standard, CBs were injected on a GC-ECD equipped with two columns. A four-level point-to-point calibration was used for quantification. PAHs were extracted in the same way and, after transfer to acetonitrile, measured using HPLC with fluorescence detection. Approximately 15 samples (5 locations) were analysed by an external laboratory for PAHs and CBs.

Transformation of the data

Since three samples are not sufficient for calculating a standard deviation, results of different locations must be combined. This was performed by dividing each single result of a triplicate by the mean value of the three results. The new series of data, on average, equal unity. The influence of between-location differences in absolute concentrations is removed and only the sampling variation together with patchiness is left. Although no absolute value of the standard deviation is obtained, the data allow the calculation of a coefficient of variation. A disadvantage of dividing by the mean is that when one of the three results is an outlier this is also reflected in the two other results. This has been overcome by using the median instead. The data of the set of 15 subsamples was treated in the same way, but the mean or median of all 15 samples was used.

Estimating the sampling variability

Approach A

The influence of spatial differences (4 and 5) cannot be included in sampling variation because that is usually one of the reasons the samples were collected. Spatial differences can only be detected when they are larger than the possible sampling error. This is principally the chicken versus egg question. Sampling variation can only be determined properly in a homogeneous area, but such an area can only be found when the sampling variation is known. This means that quantifying sampling variation will be a little subjective.

Bearing the above in mind, and considering that in addition to the variation caused by spatial differences in 170 samples some analytical outliers will occur as well, it seems acceptable to use statistics that exclude outliers. One way is to assume a Gaussian distribution, and then subtract the 0.16 percentile from the 0.84 percentile. These percentiles represent the border of plus and minus one standard deviation. Dividing the difference between these percentiles by 2 gives the relative standard deviation for the combined dataset, not influenced by outliers.

Approach B

Many different areas are multiplely sampled and, excluding samples because of apparent patchiness, a selection of those areas with low variability can be combined to obtain a statistically significant number of data points. Although this is a very subjective approach, it must be recognized that the sampling variation obtained will always be a worst case estimate. No matter how many areas are rejected, the residue will never result in a number lower than the actual variation caused by the sampling process, provided the number of data is sufficient. (This has not yet been applied to the samples.)

Results and discussion

In Table A11.1, the results of approach A using the median to transform the data are presented in four groups. Listed are the number of samples, the 0.16 and 0.84 percentiles of the raw data (to give an impression of the measured ranges), the overall relative standard deviation and the st.dev. (peak width) calculated from the percentiles of the median normalized data.

In the 'Field-var' column the standard deviations of only the 15 samples from the Oyster Grounds are listed. Next to that, the results of the separate sampling years are given.

The pure standard deviation is quite large for some CBs, i.e., CB180. However from a distribution plot (Figure A11.1), it can be noted that this is due to only a few samples. The values calculated from the percentiles, however, show quite acceptable values which closely approach the analytical variability. The highest variation is found for compounds which generally are more difficult to measure, i.e., some CBs are interfered with by coeluting compounds and dibenz(*ah*)anthracene. In addition, a considerable number of samples have concentrations which are close to the detection limit, which will lead to extra analytical variability.

Table A11.2 has the same structure as Table A11.1, except that the data are first normalized to organic carbon. In general, no improvement was obtained. This might be due to the effect that outliers are not accompanied by a higher organic carbon content, and secondly that the range of organic carbon in the subsamples is already reduced because of the sieving. However, on inspection of the original data, several individual locations show the expected covariation, especially for CBs and PAHs.

Approach B has not been applied yet, but a more careful study of the data will allow the identification of patchy areas. A recalculation of the standard deviation after rejection of data from the patchy areas will lead to a result which is a better representation of sampling variation. In addition, data which are less than a factor of 10 above the detection limit should be excluded to reduce the influence of analytical variation on the sampling variability.

Conclusion

Using the procedure described, the sampling variation varies from 5–10% for metals, and 10–15% for CBs and PAHs for the whole area considered. These values are an upper limit, as they are not corrected for the analytical variability. Further, some patchiness is always present, but may be considered absent when it is lower then the sampling variation. Although normalization on organic carbon does not give a decrease in the overall variance considering the whole set, it does decrease the variance for many individual locations.

Table A11.1 Field variance of sieved samples.

		All data combined					Field-var exp.	Results of 1990 sampling			Results of 1993 sampling		
		n-total	16% Percentile	84% Percentile	St. dev all data %	St. dev[&] peak with %	St.dev 15 samples %	n	St. dev all data %	St. dev[&] peak with %	n	St. dev all data %	St. dev[&] peak with %
LOI	%	171	10	17	9	4	4	57	7	4	114	10	5
C	%	171	2	3	12	6	5	57	13	4	114	11	7
Al	g/kg	114	30	50	8	4	5	0	nd	nd	114	8	4
As	mg/kg	171	11	22	13	8	6	57	15	8	114	13	8
Cd	mg/kg	102	0.43	1.07	24	9		57	21	10	45	27	7
Cr	mg/kg	171	58	84	9	5	4	57	11	6	114	7	4
Cu	mg/kg	171	15	24	12	6	6	57	12	8	114	12	6
Hg	mg/kg	171	0.09	0.46	17	7	6	57	19	8	114	15	6
Ni	mg/kg	171	19	32	9	5	4	57	10	5	114	8	5
Pb	mg/kg	171	36	70	15	7	7	57	18	6	114	13	7
Zn	mg/kg	171	100	189	12	7	4	57	14	7	114	10	6
PCB101	µg/kg	171	0.6	2.1	25	10	22	57	27	10	114	23	10
PCB105	µg/kg	171	0.3	1.0	45	10	7	57	72	12	114	21	9
PCB118	µg/kg	171	0.5	2.1	22	8	7	57	25	8	114	20	8
PCB138	µg/kg	171	0.6	3.0	26	11	8	57	33	10	114	21	12
PCB153	µg/kg	170	0.7	4.1	31	9	8	56	46	8	114	20	9
PCB170	µg/kg	171	0.2	1.1	59	13	15	57	97	12	114	22	16
PCB18	µg/kg	132	0.4	1.5	32	18	26	48	28	14	84	34	19
PCB180	µg/kg	171	0.2	1.6	93	12	13	57	160	13	114	18	10
PCB187	µg/kg	171	0.3	1.4	57	10	8	57	96	11	114	18	10
PCB28	µg/kg	171	0.7	2.5	32	12	14	57	30	13	114	34	13
PCB31	µg/kg	138	0.5	1.7	42	15	19	54	50	14	84	37	16
PCB44	µg/kg	171	0.3	0.8	41	11	11	57	58	11	114	29	12
PCB52	µg/kg	171	0.4	1.2	35	10	11	57	47	10	114	26	10
Ant	µg/kg	171	7	28	21	11	6	57	20	11	114	22	11
BaA	µg/kg	171	23	71	19	8	5	57	20	9	114	19	8
BaP	µg/kg	171	27	77	17	9	7	57	17	9	114	18	9
BbF	µg/kg	170	48	140	18	10	10	57	17	9	113	19	10
BeP	µg/kg	141	31	88	15	6	4	57	17	9	84	14	6
BghiPe	µg/kg	170	36	100	18	9	10	57	15	8	113	20	11
BkF	µg/kg	170	24	65	17	10	13	57	16	9	113	17	10
Chr	µg/kg	170	29	85	21	10	16	57	18	8	113	22	10
dBahA	µg/kg	141	5	17	21	11	28	57	17	10	84	23	13
Fen	µg/kg	170	49	120	18	8	7	57	15	11	113	20	7
Flu	µg/kg	171	58	190	19	7	4	57	16	7	114	21	8
InP	µg/kg	154	48	130	18	10		57	16	9	97	19	10
Pyr	µg/kg	170	44	129	25	9	4	57	17	10	113	28	8

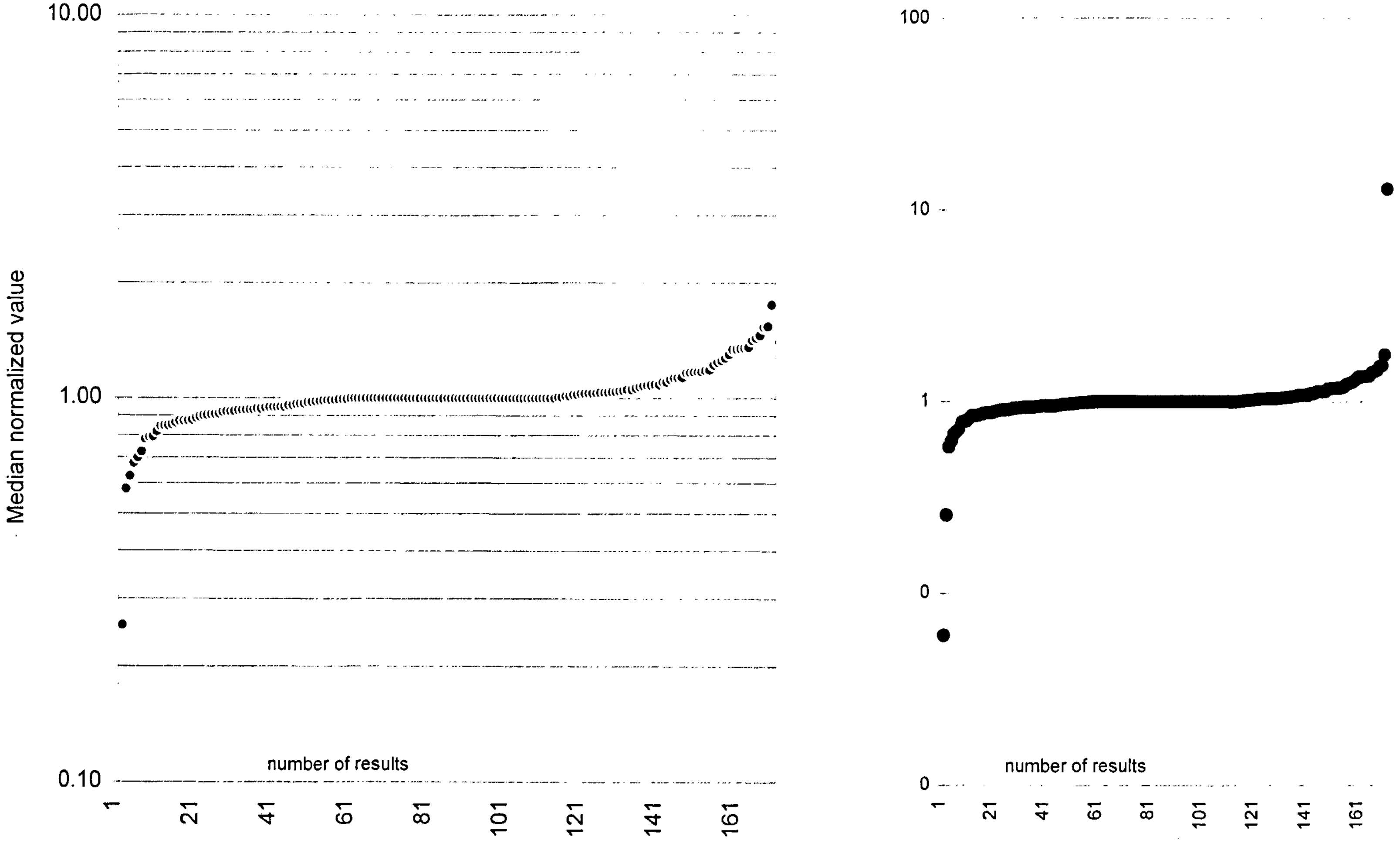
[&] this is the difference between the 0.84 and the 0.16 percentile of the median normalized data devided by 2. wich equals the standard deviation of a normal distribution. In that way outliers caused by patchiness can be excluded

Table A11.2 Field variance of sieved samples after expressing the data on organic carbon.

		All data combined					Field-var exp.	Results of 1990 sampling			Results of 1993 sampling		
		n-total	16% Percentile	84% Percentile	St. dev all data %	St. dev[&] peak with %	St.dev 15 samples %	n	St. dev all data %	St. dev[&] peak with %	n	St. dev all data %	St. dev[&] peak with %
LOI	%	171	10	17	8	5	4	57	10	5	114	7	4
C	%	171	2	3	n.a.	n.a.	n.a.	57	n.a.	n.a.	114	n.a.	n.a.
Al	g/kg	114	30	50	8	6	6	0	nd	nd	114	8	6
As	mg/kg	171	11	22	12	7	7	57	13	7	114	11	7
Cd	mg/kg	102	0.43	1.07	22	8		57	20	10	45	25	8
Cr	mg/kg	171	58	84	7	6	6	57	5	5	114	8	6
Cu	mg/kg	171	15	24	8	6	7	57	10	6	114	7	5
Hg	mg/kg	171	0.09	0.46	14	7	6	57	15	9	114	14	6
Ni	mg/kg	171	19	32	7	5	5	57	6	6	114	7	5
Pb	mg/kg	171	36	70	10	6	8	57	12	6	114	8	7
Zn	mg/kg	171	100	189	7	6	6	57	9	5	114	6	7
PCB101	µg/kg	171	0.6	2.1	24	11	21	57	28	10	114	22	11
PCB105	µg/kg	171	0.3	1.0	44	9	8	57	71	14	114	20	8
PCB118	µg/kg	171	0.5	2.1	20	9	9	57	22	9	114	19	9
PCB138	µg/kg	171	0.6	3.0	25	8	9	57	32	9	114	20	8
PCB153	µg/kg	170	0.7	4.1	29	6	9	56	45	8	114	17	6
PCB170	µg/kg	171	0.2	1.1	59	12	17	57	97	11	114	22	12
PCB18	µg/kg	132	0.4	1.5	29	18	28	48	30	13	84	29	20
PCB180	µg/kg	171	0.2	1.6	93	10	14	57	159	15	114	18	8
PCB187	µg/kg	171	0.3	1.4	57	8	10	57	96	10	114	16	8
PCB28	µg/kg	171	0.7	2.5	28	11	16	57	31	10	114	27	11
PCB31	µg/kg	138	0.5	1.7	40	15	21	54	54	11	84	28	20
PCB44	µg/kg	171	0.3	0.8	42	12	12	57	63	9	114	25	14
PCB52	µg/kg	171	0.4	1.2	36	8	12	57	52	7	114	24	9
Ant	µg/kg	171	7	28	20	11	7	57	12	11	114	23	12
BaA	µg/kg	171	23	71	16	10	6	57	13	7	114	17	11
BaP	µg/kg	171	27	77	15	11	8	57	12	6	114	17	13
BbF	µg/kg	170	48	140	15	9	10	57	11	6	113	16	10
BeP	µg/kg	141	31	88	12	7	5	57	10	7	84	13	7
BghiPe	µg/kg	170	36	100	16	8	10	57	10	6	113	18	10
BkF	µg/kg	170	24	65	15	9	13	57	10	8	113	17	10
Chr	µg/kg	170	29	85	18	10	16	57	13	8	113	20	11
dBahA	µg/kg	141	5	17	18	11	29	57	11	7	84	22	12
Fen	µg/kg	170	49	120	17	9	7	57	11	8	113	19	10
Flu	µg/kg	171	58	190	16	9	6	57	10	8	114	18	11
InP	µg/kg	154	48	130	15	8		57	11	9	97	17	9
Pyr	µg/kg	170	44	129	21	11	6	57	13	8	113	24	12

[&] this is the difference between the 0.84 and the 0.16 percentile of the median normalized data devided by 2. wich equals the standard deviation of a normal distribution. In that way outliers caused by patchiness can be excluded

Figure A11.1 Distribution plots of CB180 on two different Y-scales. In the left graph it is clear that the majority of the data range between 0.9 and 1.1. In the right graph the few outliers are visible.



ANNEX 12

ANALYTICAL VARIANCE OF THE DETERMINATION OF TRACE METALS IN MARINE SEDIMENTS

The following information was extracted from the report of the 4th QUASIMEME round of intercomparison exercises. It provides summary statistics for the determinations of a range of trace metals in two sediment samples. Two samples of sediment were analysed for a range of compounds. Generally about 30–40 laboratories reported results. The CV% values given below are robust interlaboratory coefficients of variation.

	Units	Assigned values	Between lab CV%	Assigned values	Between lab CV%
Aluminium	%	6.9	19.8	3.5	17.2
Arsenic	mg/kg	16.1	23.7	15.1	20.1
Cadmium	µg/kg	1942.0	19.9	1425.0	16.2
Chromium	mg/kg	352.0	17.2	81.8	28.3
Copper	mg/kg	187.0	14.2	24.0	13.6
Lead	mg/kg	242.3	17.4	50.5	9.8
Mercury	µg/kg	692.5	12.8	382.0	14.9
Nickel	mg/kg	55.4	15.3	20.8	20.1
Zinc	mg/kg	669.0	8.7	170.0	8.8

Variance of sediment analyses

This data summarizes the analyses of groups of 9 samples around a 500 m square at each of 7 locations, as determined by the Marine Laboratory, Aberdeen. The table also includes CV% values of the metal-to-aluminium ratios.

	C%	Al %	Cu µg/g	Zn µg/g	Pb µg/g	Cd µg/g	Hg µg/g	Cr µg/g	Ni µg/g	As µg/g
Hebrides										
mean	0.43	3.46	7.25	45.05	23.59	0.02	0.05	57.51	6.32	4.26
std dev	0.09	0.38	1.16	7.58	2.57	0.01	0.02	8.90	2.97	0.43
CV	21.29	11.07	15.96	16.83	10.89	40.22	41.49	15.47	47.08	10.12
CV of M/Al			17.48	19.52	14.05	44.72	31.01	17.07	42.72	16.16
Solway										
mean	0.46	2.72	7.11	63.01	28.50	0.05	0.06	46.35	5.70	7.51
std dev	0.10	0.59	0.75	4.66	1.91	0.00	0.01	9.11	3.98	0.80
CV	22.10	21.78	10.59	7.40	6.71	8.03	18.76	19.66	69.72	10.70
CV of M/Al			24.85	23.71	22.99	23.85	30.01	27.01	71.72	22.89
Clyde										
mean	1.07	5.83	17.53	126.12	49.29	0.13	0.10	94.34	23.78	9.54
std dev	0.05	0.86	0.52	3.96	2.14	0.02	0.01	7.01	2.01	1.34
CV	4.69	14.76	2.97	3.14	4.35	19.40	10.21	7.43	8.45	14.05
CV of M/Al			14.32	14.80	13.47	21.16	19.74	17.47	15.99	24.19
Moray Firth										
mean	1.92	4.64	9.90	69.96	34.20	0.09	0.08	52.60	9.48	4.56
std dev	0.19	0.95	2.30	10.63	5.46	0.02	0.02	11.37	3.61	0.75
CV	9.88	20.37	23.27	15.19	15.96	20.29	25.33	21.62	38.11	16.42
CV of M/Al			16.86	18.09	19.14	33.22	17.65	20.49	21.33	13.51
Moray Firth										
mean	0.27	3.13	3.35	18.14	19.68	0.06	0.05	18.08	0.00	1.48
std dev	0.06	0.42	0.54	2.64	2.42	0.01	0.01	6.70	0.00	0.63
CV	23.82	13.43	16.05	14.57	12.31	18.01	25.59	37.09	-	42.46
CV of M/Al			16.59	13.64	12.70	15.45	32.12	35.38	-	46.67
Forth (offshore)										
mean	0.41	3.26	2.47	16.22	19.70	0.01	0.07	16.02	0.00	8.31
std dev	0.06	0.28	0.34	1.06	1.11	0.00	0.02	5.29	0.00	2.93
CV	14.67	8.50	13.63	6.54	5.61	69.30	26.81	33.02	-	35.31
CV of M/Al			13.52	9.39	8.91	68.47	26.86	36.95	-	36.81
Tay (offshore)										
mean	0.28	4.79	4.54	38.30	24.30	0.26	0.05	45.27	0.00	6.87
std dev	0.06	0.59	0.27	2.81	1.64	0.05	0.01	4.18	0.00	0.74
CV	21.16	12.24	5.95	7.34	6.75	18.02	17.69	9.22	-	10.82
CV of M/Al			13.59	16.60	15.07	25.01	25.14	19.19	-	21.45

ANNEX 13

RECOMMENDATIONS

To Council

The WGMS recommends that:

1) A meeting of WGMS should be held for 4 days in March 1997 concurrent with WGBEC at ICES Headquarters in Copenhagen, Denmark, to:

    a) prepare a technical annex on PAH analysis in sediments for the sediment guidelines (in collaboration with MCWG);

    b) review and report on results of recent surveys on nutrient cycling between sediment and water, in particular with respect to the denitrification potential and secondary pollution potential for phosphate;

    c) review available data which may help in establishing normalizers for organic contaminants;

    d) report on the statistical assessment of data on time series monitoring in sediments (in collaboration with WGSAEM);

    e) review and report on biogeochemical processes which might change speciation and mobility of trace metals in sediments;

    f) review methods for investigating the processes of particle-water interaction of organic contaminants;

    g) review available data on the fate of fish farm medicines in sediments;

    h) review new data on toxicological effects of PAHs in sediments, in particular with regard to changes in benthic community structure;

    i) meet with WGBEC to develop areas of mutual interest that might be pursued by JMSBEC;

To ACME

The WGMS recommends that:

1) ACME adopt Annex 7 on CB analysis in sediments to be included as a technical annex to the ICES/JMP sediment guidelines.

To the ICES Secretariat

The WGMS recommends that:

1) ICES should ask the Danish delegate to invite for the next meeting of the Working Group an expert to present the most recent results of research in nutrient cycling between sediments and water, e.g., Dr Lomstein from Aarhus University;

2) the Environment Department draft a report on the statistical assessment of data on time series monitoring in sediments.